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合成樹脂塗料に依る浮子の防水効果について

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On the Coating Effect of Synthetic Resin Paint for the Float

Yongjun PACK

This study was attempted to investigate the coating effect of the wooden float. Three kinds (following A, B, C) of wooden pieces made of paulowania, Japanese cypress and birch being used commonly as the wooden float were selected, and five pieces were employed to each run as the test pieces.

A. The wooden pieces dried in an oven for 3 hrs at 100°C after being cut into a dimension of $10 \times 10 \times 20\,mm^3$.

B. The wooden pieces coated with synthetic resin paint five times for the test pieces-A.

C. The wooden pieces impregnated, for 5 hrs under pressure of 5 atm by a compressor, with low condensation phenol resin which has resin content 20.2 %, specific gravity of 1.060 and specific viscosity of 2.49, then coated by the same method as in the case of the test pieces-B.

Table 1 shows the weight of synthetic resin which coated the test pieces-B and-C and of the resin impregnated in the test pieces-C.

The test pieces treated by the above mentioned methods were then allowed to soak in the sea water the temperature of which was regulated at 30°C, and then absorption of water was measured by the increment of weight.

The amount of absorbed water W after being soaked for t hours may be represented by the following emprical expression;

$$W=W_{I}(1-e^{-\alpha_1 t})+W_{II}(1e^{-\alpha_2 t}),$$

where W_I, W_{II}, α_1 and α_2 are constant.

The difference of the mode of absorbing process with the treatments can be seen in Fig. 1 and Table 2.

1. The coating effect of the test pieces treated only with synthetic resin paint or both the resin paint and the resin was effective distinctively as compared with the untreated ones.
2. An appreciable effect due to impregnation could not be seen, but this treatment caused shrinkage and warpping of the test pieces.
3. All the untreated test pieces sunk thoroughly within a month after soaking, but the treated ones were floating during three months under this experiment.

浮子は浮力の大なることが最も重要であるが，浸漬に依る吸水及び腐蝕性の少いこと，堅牢にして破損し難く，且つ安価に入手し得ると云うことも又重要である。従来久しく使用されてきている竹，桐，檜，松，杉等の木製の浮子に代つて近年ガラス製，鉄製，各種合成物質製等の浮子がより合理的なものとして作られ且つ実用化されつゝある。然しガラス製，鉄製共に浮力は非常に大であるが，ガラス製は破損し易く，鉄製は価格が高い。又合成物質製の中には浸漬時水圧に依る吸水の大なるものが多く，一定水深以下では浮子として使用し難い事，価格の高い事等の欠点がある。破損し難く浮力が比較的大で，しかも安価に入手し得るのは今日なお依然として多量に使用されている竹，桐等であろう。そこで筆者は桐，檜，樺等の三種の木材が海水に浸漬されたとき，吸水に依る浮力の減退を小にするための一方法として，これらの木材を合成樹脂塗料

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（ビニール系）及び低縮合石炭酸樹脂等にて処理し，これに依る防水効果の程度を調べるために本実験を行つた。

実　験　方　法

試験片の作製：試験片としては桐，檜，樺等の三種の木材を次記の如く，三様に処理した後，各材について各処理法毎に五片づゝ撰んで採用した。

A.　充分に風乾された桐，檜，樺等の三種の木材を平滑にするために鉋をかけ，表面の相異から生ずる実験誤差を出来るだけ小にするため各材の木目の一様な部分を撰び，大きさ $10\times10\times20\,mm^3$ に切断して約36時間，100°C の乾燥器中にて絶乾状態に乾燥した木片。

Table 1. The weight of coated synthetic resin paint and low condensation phenol resin impregnated (Unit; g)

Specimen \ Weight	Weight of five specimens	Amount of paint	Amount of resin
Paulowania	2.715	1.315	1.764
Japanese cypress	4.305	1.384	1.554
Birch	6.819	1.385	1.198

B.　試験片 A に所定の方法[1] で合成樹脂塗料を5回塗装した木片。

C.　試験片 A に所定の方法[2] で作られ，含脂率20.2%，比粘度 24，比重 1.060 の低縮合石炭酸樹脂を 5 Atm の加圧下で5時間注入した後，100°C の乾燥器中にて約7時間熱硬化させ，試験片 B の場合と同様回数塗装した木片。この熱硬化は樹脂の水中への溶出を防ぐと同時に，木材中での完全な防水膜を形成させるためである。なお注入樹脂として上記の性質を有する低縮合石炭酸樹脂を使用したのは，木材組織中での樹脂形成能が最も大きいからである[3]。

塗装法：試験片 B 及び C の作製時，合成樹脂塗料（ビニール系）を塗装したが，その方法は所定の要項[1] に従い，塗装間隔は約 24 時間，塗装間の乾燥は蔭乾し，風乾した。Table 1 は塗装前の試験片 1g 当りの重さに附着した塗料及び注入した樹脂の重さを示すが，これに依ると，総塗料量は各材の試験片について約 1.3g で略々等量であるが，単位重量に対する塗料量は各々異つていて，それは桐，檜，樺の順に大きく，又総注入樹脂量及び単位重量に対する樹脂量はそれぞれ桐，檜，樺の順に大きい。

測定：上記の方法で作製，塗装された各試験片に標識を附し，30°C の空気恒温槽中に準備された海水中に 96 日間浸漬した。こゝに標識は処理法即ち未処理（試験片 A）の場合，合成樹脂塗料だけで処理した（試験片 B）場合及び合成樹脂塗料と低縮合石炭酸樹脂との両者で処理した（試験片 C）場合をそれぞれ A，B，C 等の記号で，桐，檜及び樺等の材料（木種）に依る区別は添字 1，2，3 をそれぞれ附して表わした。吸水量の測定は，1955 年8月 26 日から同年 11

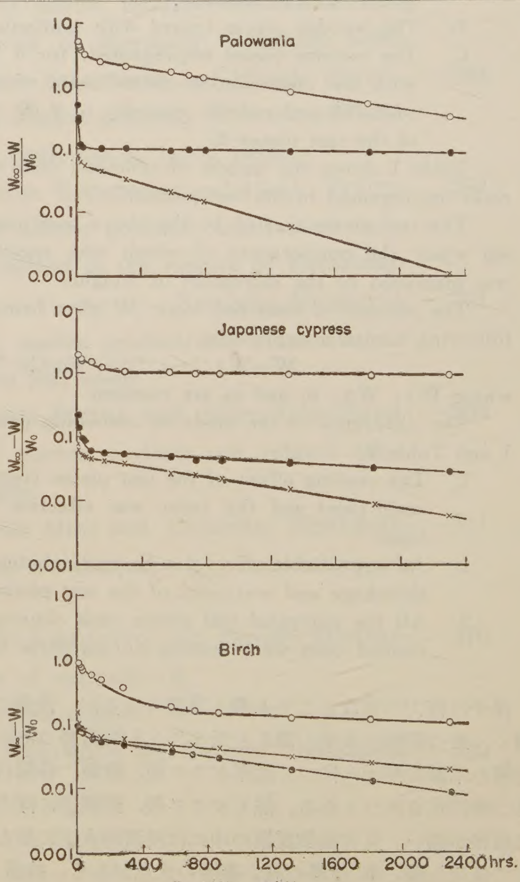


Fig. 1. Relation between absorption of water by each specimen and soaking period. Symbol ○, ● and × show the test specimen -A, -B and -C respectively

月 30 日までの間 13 回にわたつて，試験片の表面に附着した水分を濾紙で拭きとつた後行つた。

なお各試験片のある時刻 t における吸水割合 W はその試験片のその時刻 t に於ける吸水浮子の重量 w (g) からその試験片の海水浸漬時の重さ w_0(g) を差引いた重さを w_0 で除し，$W=\frac{w-w_0}{w_0}$ で算出した。Fig. 1 は各試験片の飽和吸水量 w_∞ から各時刻 t における吸水量 w (g)を差引いた g 当りの対数値 $log\frac{w_\infty-w}{w_0}$ と浸漬時間 $t(hr)$ との間の関係を示す。

実験結果及び考察

試験片が海水に浸漬された時，吸水は先づ木材中の大きな空隙部分に対して急激に行われ，比較的短時間の間に此の部分は飽和してしまい，次第に実質部分に向つて吸水が行われるものとし，吸水量は長時間の後には飽和状態に達するものと思われる。

今木材の空隙部分及び実質部分への吸水量をそれぞれ W_I，W_{II} とし，W_I 及び W_{II} 部分への浸水係数をそれぞれ α_1 及び α_2，浸漬時間を t で表わした場合には単位重量に対する総吸水量 W は次式に依つて表し得る[4]。

$$W=W_I(1-e^{-\alpha_1 t})+W_{II}(1-e^{-\alpha_2 t})$$

Table 2 は定数 W_I，W_{II}，α_1，α_2 と実測から得た総吸水量 W 及び飽和吸水量 W_∞ 等を示し，これらはもとの試験片 1g 当りの重さに対するそれぞれの値を表わしている。なお飽和吸水量 W_∞ は次式に依つて計算した。

$$W_\infty=\frac{w_1\times w_3-(w_2)^2}{w_1\times w_3-2w_2}$$

こゝに w_1，w_2 及び w_3 は浸漬時間 t_1，t_2 及び t_3 を等間隔に取つた時，それぞれの時刻に対する吸水量を示す。

Table 2. Absorption of water by test pieces

Specimen \ Absorption of water	W_∞	$W_{t=2304}$	W_I	α_1	W_{II}	α_2
A_1	4.051	3.852	1.323	0.00035	2.728	0.00062
B_1	0.163	0.095	0.103	0.00021	0.060	0.00004
C_1	0.125	0.125	0.065	0.00082	0.059	0.00076
A_2	2.411	1.837	1.377	0.00041	1.034	0.00005
B_2	0.229	0.179	0.173	0.00077	0.056	0.00023
C_2	0.062	0.057	0.024	0.00043	0.038	0.00053
A_3	1.134	0.915	0.772	0.00062	0.361	0.00021
B_3	0.085	0.078	0.031	0.00095	0.054	0.00040
C_3	0.108	0.081	0.025	0.00049	0.083	0.00029

W_∞; Absorption of water in infinity. W_t; The weight of test specimens after being soaked for 2304 hrs. W_I and W_{II}; Absorption of water of multiperforated part and solid part respectively. α_1 and α_2; Coefficient of absorption of water by W_I and W_{II} part respectively.

次に処理に依る防水効果をより詳細に検討するために，それぞれの試験片について，未処理の試験片の単

Table 3. Relation between the ratio of absorbed water of test pieces-B and -C to pieces-A and three kinds of absorption of water W, W_I and W_{II}

Ratio \ Absorption of water	W	W_I	W_{II}
B_1/A_1	0.02466	0.07785	0.02199
C_1/A_1	0.03245	0.04535	0.02162
B_2/A_2	0.09745	0.12563	0.05415
C_2/A_2	0.03103	0.01743	0.03675
B_3/A_3	0.07352	0.04015	0.14915
C_3/A_3	0.07634	0.03238	0.22931

W; Total amount of absorbed water. W_I and W_{II}; Absorption of water by multiperforated part and solid part respectively.

位吸水量に対する処理の試験片のそれの比を求めた。Table 3 はその結果を示す。これに依ると処理に依る防水効果は桐材に於て最も顕著に現われ，次いで檜，樺の順に大きく，さらに同一の試験片に於ては桐材の場合には実質部分（W_{II}）に，樺材の場合には空隙部分（W_I）により大きく現われ，檜材の場合には判然としないようである。

以上の測定結果から次の事柄がわかる。

1. 飽和吸水量は未処理（A_1～A_3）の場合には処理した場合（B_1～B_3，C_1～C_3）に比べて非常に大で，合成樹脂塗料に依る木製浮子の防水効果は顕著であり，それは桐，檜及び樺の順に大きい。

2. 合成樹脂塗料だけで処理した（B_1～B_3）場合と，低縮合石炭酸樹脂を木材中に注入し，かつ合成樹脂塗料にて処理した（C_1～C_3）場合との防水効果の差異はあまり顕著でないが，檜材の場合には後者がより良い効果を示した。併し木材を熱硬化する時，反り，割れ，峰窩等が生ずるがこれらを防止し得るならば，より大きい効果があるのではないかと思われた。

3. 吸水量の計算に依つても言い得る事であるが，観察によると未処理の試験片（A_1～A_3）は海水浸漬後一個月以内に浮力を失つて完全に沈降したが，合成樹脂塗料にて処理した試験片（B_1～B_3，C_1～C_3）は三個月後の実験修了時にも依然として浮上していた。

尚，終りに本実験に当つて御指導並びに論文の御校閲を賜つた当教室川上太左英教授，実験準備に御指導並びに御援助を御願いした京都大学農学部梶田茂教授，山田正助手，京都大学木材研究所後藤輝雄講師，当教室岸本昭助手及び合成樹脂塗料の提供を快諾して下さつた日本ペイント研究所長辰已佐一氏に深謝の意を表する。

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日本産ウシノシタ魚類の成長について

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On the Growth Pattern of the Soleoid Fishes Taken Mainly from Southern Part of Japan

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The growth differentiation found among 19 Japanese soles obtained from southern part of Japan is quantitatively viewed with several biological aspects.

At the age of 3 years, the body reaches 100 mm or even becomes longer in the fishes belonging to the subfamily Synapturinae, but in those of the other subfamilies of Soleidae (Soleinae and Achirinae) it is usually shorter. In the family Cynoglossidae, the members of the subfamily of Cynoglossinae attain on the whole more than 100 mm in the body length, whereas the fishes of the Symphirinae never reach 100 mm.

According to extremity body length calculated by the difference diagram, each of the tropical, subtropical and temperate forms is clearly divided into 3 groups. But the tropical form is always more or less longer than the others (Fig. 3). It also seems probable that in the same genus the species originated in the tropical ocean have a longer body than the endemic ones of Japan and China (*i.e.* : *Zebrias zebra*–*Z. japonicus*, *Aseraggodes kaianus*–*A. kobensis*, *Symphurus strictus*–*S. orientalis*).

There is a tendency in this group that the higher counts anal soft rays the fish has, the larger the body becomes.

水産資源の調査が広く行われるようになつてから，多くの魚類の成長が次第に明らかとなつてきた。成長率は年令組成・生残率等と関連しているばかりでなく，種の分化を解明するうえにもしばしば有力な手がかりとなることがある。一つの属または科内の種類の成長状態を調査すると，多くの場合二つないしそれ以上の群に分かれる。そしてその場合近似種の矮小型と巨大型との間には，形態上の分化が成長の分化と関連して起つたと考えられる場合がしばしばある。

筆者はここで日本産ウシノシタ類 19 種の成長状態が，分類学上の地位，地理的分布及び形態上の差異などとどのような関係にあるかを究明したい。ウシノシタ魚類は，分類学上ササウシノシタ科とウシノシタ科に分けられる。ササウシノシタ科中，シマウシノシタ属，ツノウシノシタ属などはシマウシノシタ亜科に属する。ウシノシタ科はウシノシタ亜科とアズマガレイ亜科とに分けられる。ここでササウシノシタ科とシマウシノシタ科とを一括したのは，これらが分類学上近縁であるばかりでなく，何れも暖流系のもので同じ様な生態・習性を持つからである。

調査個体は主として外洋性の南部太平洋沿岸各地から 1950—1954 年の 1 ～ 3 月の間に，手繰船で漁獲されたものである。年令決定は有眼体側肩部の鱗によつた。年輪形成時の体長は鱗径と体長の回帰関係から推定した。また，各種の分布をあらわす指数として，これらの分布の北限と南限の緯度の平均値を用いた。これを生物学的緯度と呼び，20 より小さいものを熱帯性種，30 前後のものを亜熱帯性種，33 より大きいものを温帯性種と呼ぶことにする。更に，日本産ウシノシタ類は地理的分布から本土系（本邦近海にのみ棲む)，支那系（支邦大陸沿岸及び日本近海)，熱帯大洋系（熱帯地方及び外洋性南部太平洋）及びコスモポリタン系（印度洋・太平洋にかけて広く分布する）に 4 分される。

本研究をすすめるにあたつて，ご指導を賜わり本稿を校閲して下さつた松原喜代松教授に厚くお礼を申し上げる。なお，この研究は文部省科学研究費の一部によつて行われたものである。

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研　究　結　果

日本産ウシノシタ類 19 種の年令別平均体長は，種類によって著しい差異がみられるが，それでも成長状態によって4型に分けられる（Table 1～2)。第1型にはオオシタビラメがふくまれ，満1年で 200 mm，2年で 300 mm，3年で 360 mm，4年で 400 mm 内外に達する。第2型にはクロウシノシタ，イヌノシタ，

Table 1. Standard length of each age computed from scales, estimated extremity body length, and the longest body length in samples of Japanese dextral soles

Species	Form	Standard length in each age (mm) 1	2	3	4	Extremity body length (mm)	Longest body length (mm)
Pardachirus pavoninus ミナミウシノシタ	Cosmopolitan	100.0	148.0	—	—	—	—
Zebrias fasciatus オビウシノシタ	Chinese	82.0	135.3	176.5	196.0	290.0	217
Aesopia cornuta ツノウシノシタ	Cosmopolitan	90.0	140.0	—	—	—	—
Zebrias zebra シマウシノシタ	Cosmopolitan	67.5	103.8	125.6	155.5	210.0	187
Zebrias japonicus セトウシノシタ	Japanese	65.5	96.2	118.4	—	173.0	143
Heteromycteris japonicus ササウシノシタ	Chinese	60.9	81.0	92.0	—	108.0	128
Aseraggodes kaianus モヨウウシノシタ	Tropical	48.0	90.0	—	—	—	—
A. kobensis トビササウシノシタ	Japanese	48.6	64.0	78.3	—	116.0	101

Table 2. Standard length of each age computed from scales, estimated extremity body length, and the longest body length in samples of Japanese sinistral soles.

Species	Form	Standard length in each age (mm) 1	2	3	4	Extremity body length (mm)	Longest body length (mm)
Arelia bilineata オオシタビラメ	Cosmopolitan	203.2	303.0	363.0	397.0	440.0	431
Cynoglossus robustus イヌノシタ	Chinese	136.2	221.0	261.7	311.3	400.0	393
Rhinoplagusia japonica クロウシノシタ	Chinese	122.0	203.2	272.0	—	420.0	334
Areliscus trigrammus ムラサキシタビラメ	Chinese	123.0	205.0	258.8	—	400.0	327
Paraplagusia blocki ナツヨウウシノシタ	Cosmopolitan	104.0	160.0	—	—	—	—
Areliscus joyneri アカシタビラメ	Chinese	98.5	142.5	166.2	210.3	325.0	245
Areliscus sp. ヒレグロゲンコ	—	93.5	135.8	172.5	200.3	325.0	215
Areliscus interruptus ゲンコ	Chinese	71.5	104.0	135.2	154.3	245.0	172
Symphurus strictus ヒモウシノシタ	Tropical	72.0	100.4	110.1	—	113.0	131
S. orientalis アズマガレイ	Chinese	60.6	86.5	—	—	—	—
Areliscus itina リュウキュウウシノシタ	Japanese	50.0	71.2	87.2	102.9	150.0	143

ムラサキシタビラメの3種がふくまれ，1年で 130 mm，2年で 210 mm，3年で 260 mm，4年で 300 mm 前後になる。第3型にはミナミウシノシタ，ナンヨウウシノシタ，アカシタビラメ，ヒレグロゲンコ，オビウシノシタ及びツノウシノシタなどが属し，1年で 100 mm，2年で 140 mm，3年で 180 mm，4年で 200 mm 前後に達する。第4型は矮小形のウシノシタ類であつて，シマウシノシタ，ゲンコ，セトウシノシタ，ヒモウシノシタ，モヨウウシノシタ，アズマガレイ，ササウシノシタ，リュウキュウシノシタ，トビササウシノシタなどがふくまれる。これでも分るように，ウシノシタ亜科にふくまれる種類の成長的分化は著しくて4型の何れにも属するが，アズマガレイ亜科は矮形で，第4型にのみ属する。ササウシノシタ科の魚類は一般に小形であつて，大部分のものは第4型に属している。そしてこの科内では，シマウシノシタ亜科のものがトビササウシノシタ及びササウシノシタ

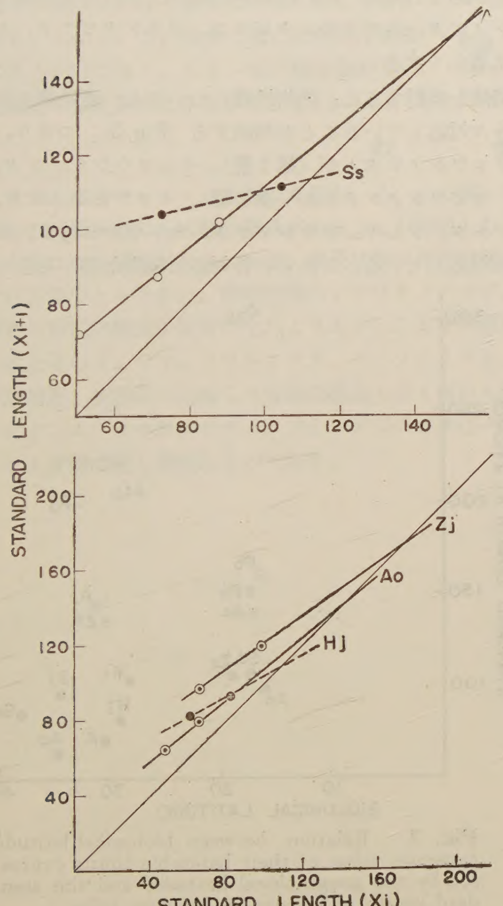


Fig. 1. Extremity body length estimated by the difference diagram in Japanese soles
A : *Areliscus itina.* Ao : *Aseraggodes kobensis.* Hj : *Heteromycteris japonicus.* Ss : *Symphurus strictus.* Zj : *Zebrias japonicus.*

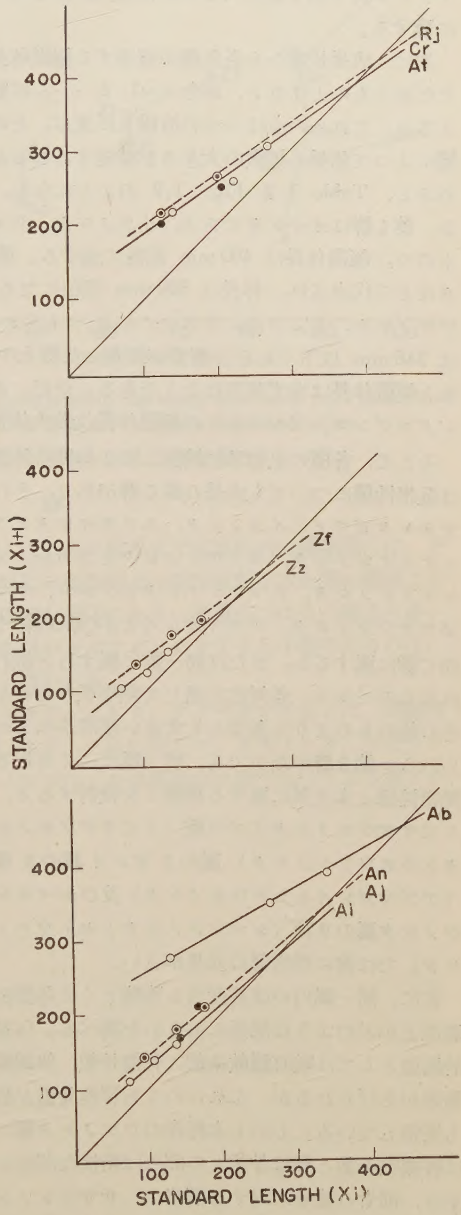


Fig. 2. Extremity body length estimated by the difference diagram in Japanese soles
Ab : *Areliscus bilineata.* Ai : *Areliscus interruptus.* Aj : *Areliscus joyneri.* An : *Areliscus sp.* At : *Areliscus trigrammus.* Cr : *Cynoglossus robustus.* Rj : *Rhinoplagusia japonica.* Zf : *Zebrias fasciatus.* Zz : *Zebrias zebra.*

亜科のものより一般に大きい。

ウシノシタ亜科に属する種類の成長状態は多様性をしめしたが，それでも第4型に属するものは本土系または支那系であつて，コスモポリタンまたは熱帯大洋系はすべて第1～3型にふくまれる。同様に，ササウシノシタ科中第3型に入るのは熱帯大洋系またはコスモポリタン系であつて，その他の系統のものは第4型に属する。

次に，成長状態から各魚種が到達する極限体長を定差図によつて推定することにする。体長が成長法則にしたがうものとすると，年令 $i=1, 2, \cdots\cdots$ に計測される体長 X_i について，横軸に X_i，縦軸に X_{i+1} をとると，これらの点は一つの直線上に並ぶ。その直線と横軸に原点で 45 度の傾きを持つ直線との交点の座標によつて体長の極限の大きさを推定することができる。日本産ウシノシタ類 14 種について極限体長を求めると，Table 1,2, Fig. 1,2 のようになる。これらの極限の体長によつて 14 種は次の3群に分けられる。第1群はオオシタビラメ，イヌノシタ，クロウシノシタ，ムラサキシタビラメなどによつて代表されるもので，極限体長は 400 mm 前後に達する。第2群はアカシタビラメ，ヒレグロゲンコ及びオビウシノシタなどで代表され，体長は 300 mm 前後になる。第3群にはササウシノシタ，ヒモウシノシタ，トビササウシノシタ，リュウキュウウシノシタ，セトウシノシタ，シマウシノシタ，ゲンコなどがふくまれ，極限体長は 245 mm 以下である。著者が調査した標本中の最大体長は Table 1,2 にかかげたが，これらと比較すると極限体長はまず妥当なようである。ただ，クロウシノシタ，ムラサキシタビラメ，アカシタビラメ，ヒレグロゲンコ，ゲンコなどの極限体長は最大体長よりも著しく大きい。

そこで，各種の生物学的緯度と満2年目の体長との関係を検討すると，熱帯性種についても，亜熱帯または温帯性種についても成長の異る群があり，それらが各々対応していることが判明する (Fig. 3)。つまり，オオシタビラメとイヌノシタ，ムラサキシタビラメ，クロウシノシタとが（第1群），ナンヨウウシノシタ，ミナミウシノシタ，ツノウシノシタとアカシタビラメ，オビウシノシタとが（第2群），モヨウウシノシタ，ヒモウシノシタ，シマウシノシタとゲンコ，ササウシノシタ，リュキュウウシノシタ，セトウシノシタ，トビササウシノシタ，アズマガレイとが(第3群)それぞれ対応している。これらの各対応は極限体長からみて同じ群に属するか，または同一群に属すると思われるものであり，各対応を通じて熱帯系のものがその他のものよりも多少とも大きい傾向がみとめられる。第3群のなかでも，同一属にふくまれる熱帯性種と本土系に属する種類とを検討すると，トビササウシノシタアズマ種（トビササウシノシタとモヨウウシノシタ），属の2 ガレイ 属の2 種（アズマガレイとヒモウシノシタ）及びシマノウシノシタ属の2種（シマウシノシタとセトウシノシタ）では常に熱帯種の成長がよい。

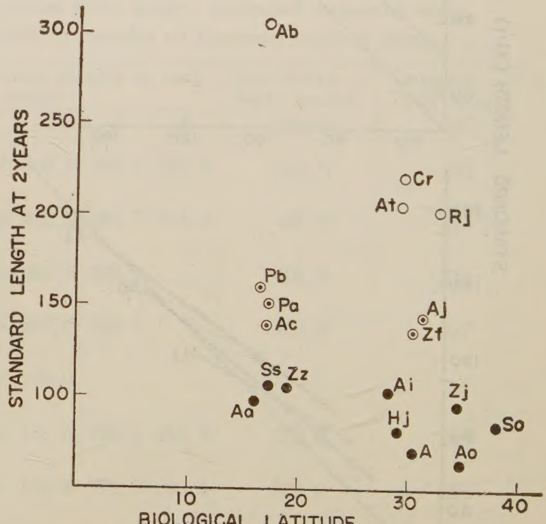


Fig. 3. Relation between biological latitude (average value of their habitable limits expressed by the geographical latitude) and the standard length at 2 years in Japanese soles
Aa : *Aseraggodes kaianus*. Ac : *Aesopia cornuta*. Pa : *Pardachirus pavoninus*. Pb : *Paraplagusia blocki*. So : *Symphurus orientalis*.
○ 1st group. ◉ 2nd group. ● 3rd group.

次に，同一属内の成長度合と形態とくに体節的構造とがどのような関係にあるかを調べる。体節的構造としては垂直鰭軟条数，脊椎骨数，側線鱗数等があげられるが，これらのうち脊椎骨数が最も安定している。しかし本邦産のウシノシタ類では臀鰭軟条数と脊椎骨数との間には密接な関係があり，前者の後者に対する割合は，ササウシノシタ科で 1.3～1.5，ウシノシタ科で 1.6～1.7 であるから，ここでは便宜上臀鰭軟条数ををもつて体節的構造を代表さすことにする。トビササウシノシタ属，シマウシノシタ属，アカシタビラメ属及びアズマガレイ属などについて，2年魚の体長

と鰭条数との関係をしらべると Fig.4 のようになる。トビササウシノシタ属の2種間では，鰭条数に差がみられないが体長にはかなりの差異がある。シマウシノシタ属ではオビウシノシタ，シマウシノシタ，セトウシノシタの順に体長が減少するが，臀鰭軟条数はオビウシノシタだけがとくに多い。アカシタビラメ属では全体として条数が増すと体長も大きくなる傾向がある。しかし，ゲンコはアカシタビラメ，ヒレグロゲンコなどと条数がほぼ等しいが，体長はそれらよりも小さい。アズマガレイ属の2種では条数と体長の増減とが相ともなう。

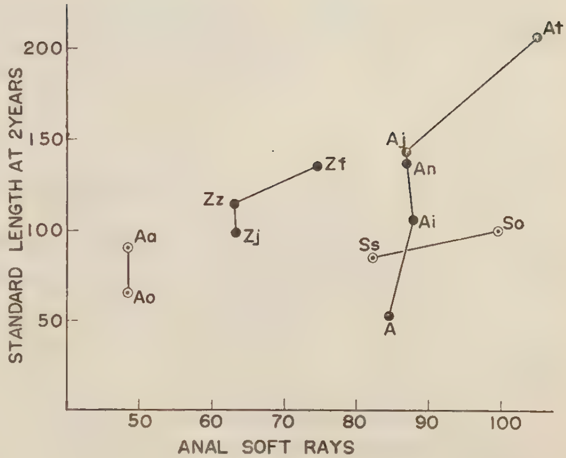


Fig. 4. Relationship between anal soft rays and standard length at 2 years in some Japanese soles

これらのことから，初期の成長と体節的構造との間にはかなり密接な関係にあることが分る。しかし，この両者は常に比例的な関係にあるわけでなく，ある一定の鰭条数をもつ種類間でも成長的な分化がみとめられるが，それにはある程度の限界があるようである。

む す び

日本近海産ウシノシタ魚類の成長をいろいろの面から解析した。その結果まず同亜科内の種類間には，それらの成長状態にある種の限界があることが判明した。また同属の種類間では熱帯性種が本土系の種類よりも大型になる傾向がある。一方，成長状態は体節的構造とも密接な関係にあり，同属内ではこの構造の多いものが多少とも大きい。熱帯性種のシマウシノシタが，亜熱帯性のオビウシノシタよりも小型であるのは，前者の体節的構造が後者のそれよりも少いことと関連があると思われる。

本土系のリュウキュウウシノシタ，セトウシノシタ，トビササウシノシタ，アズマガレイなどは，同属内の熱帯系，支那系に比較して体節的構造も少く何れも矮小型である。これに対して，イヌノシタ，オビウシノシタ，ムラサキシタビラメ，アカシタビラメ及びクロウシノシタなどの支那系は大型であつて日本産ウシノシタ資源中最も重要なものである。

カレイ類の棲息場所選択と環境の評価についての実験的研究

小坂昌也
（東北大学農学部水産学教室）

Experimental Studies on the Habitat Preference and Evaluation of Environment by Flatfishes, *Limanda yokohamae* (GÜNTHER) and *Kareius bicoloratus* (BASILEWSKY)

Masaya KOSAKA

The indiuidual fish of *Limanda yokohamae* was liberated one by one from a definite position into the experimental pool, whose bottom was provided on one side with the fine sand and the other side with the small gravel, each in half space.

The number of individuals settled on either the sand or the gravel bottom was counted at each time of the liberation. The same was done by the different species, *Kareius bicoloratus*.

The results showed that, when the population density is low, both the species tend to settle on the side of sand than gravel; however, with the increasing density, the tendency of preference for the sand gradually falls. (Figure 1)

Namely, the probabilities for the settlement on the sand are high at the lower density and decrease as the density becomes higher.

In order to find out the relationship between the habitat preference and the population density, MORISITA's theory on the environmental density and probability formula derived from its theory were applied for the analysis of the results of this experiment. The frequency distribution of the number of individuals settled on the bottom of the tank were conicident well with the expected values calculated by MORISITA's formula for both the species (Tables 2 & 3).

The values of the environmental density (expressed as the population density) were 0.10 for the sand and 3.10 for the gravel in the case of *L. yokohamae* and 0.22 for the sand and 1.95 for the gravel in the case of *K. bicoloratus*.

まえがき

自然状態ではカレイ類は，その各分布範囲内に一様に分布しておらず，局所的に集つて棲息していることが知られている。そして多くの個体が棲息している場所は，その他の場所に比較して「より好適な棲息場所」であるというようなことがいわれているが，その意味する内容は極めてあいまいで，漠然としている。そこでこのような場合に各棲息場所が持つている価値を量的に明確に表わさなければならない。評価の方法としては，これまでに多く行われているように生物の現象をしらべ，他方でそれと関係がありそうに思われるいくつかの外囲条件を測定し，両者を単に結びつけるような方法ではなくして，魚類主体を通じての環境の評価という方法が重要のように思われる。

すでに上述のような立場にたつて，森下[1]はアリジゴクを用いて実験を行い，新たに環境密度理論を提唱し，ある場所の価値は棲息密度により換算されて量的に評価できることを示した。

1955年よりカレイ類の生態をより詳細に知るために，飼育して種々の実験を行つているが，ここでは底質とカレイ類の棲息とはどのような結びつきをもつているか，或は底質の異なる二つの場所（底質の差異ということは，自然水域では単に粒子の物理的差異のみならず，その場の海底流・海底地形の差異及びそこに棲息

1956年7月3日受理

する生物種が異なり生産構造にも違いがあると考えられるので使用した。)がカレイ類にとつて，どのような価値をもつているかを知るために実験を行い，その結果を森下の理論を適用して考察を行つた。

本実験に際し終始御指導を賜わり，御校閲下された畑中正吉博士と実験を行う上に御便宜を与えて下さつた松島水族館高橋良夫館長並びに同竹内健氏に深く感謝する。

材　料・方　法

実験魚としてカレイ類のうちでも比較的沿岸性のマコガレイとイシガレイを使用した。両種とも松島湾内の簀建で漁獲された個体を松島水族館のコンクリート水槽中で 11 月初より飼育実験を行つたもののうち，マコガレイ 12 尾（体長 16.1～22.1 cm）イシガレイ 8 尾（14.7～25.7 cm）を使用して 1955 年 12 月初旬に実施した。

実験水槽としてコンクリート水槽（80×45×17cm）の内面にうすいクリーム色の塗料を塗つたものを用い，第 1 表に示すような大きさの砂と小石を底に等面積に約 4cm の高さにしき，海水を約 15cm の高さまで注入し実験中時々両部分に空気を送つた。実験中の海水温は 8.2～11.2°C であり，光・温度等の条件は両部分においてできるだけ差のないようにした。

Table 1. Mechanical analysis of the sand and the gravel used in this experiment

Sand		Gravel		
Diameter			Longer Diameter	Shorter Diameter
>2.8mm	2.1%	mm		
2.8～1.4	7.2	20～10	21	0 %
1.4～0.7	15.8			
0.7～0.35	64.1			
0.35～0.15	10.3			
0.15～0.075	0.5	10>	79	100
0.075>	0.0			

場所の選択と密度の関係

1.　マコガレイ

まず 1 個体を砂と小石の両部の境界線上の水中で放すと，いずれか一方に潜入定着する。実験は 32 回行つたがそのうち半数は砂が魚体の進行方向左側になるようにし，半数は右側になるようにした。その結果は両者を通じて 32 回中 31 回が砂側へ定着し，小石側へ定着したのは，ただの 1 回のみである。要するにマコガレイが小石側より砂側に多く定着するのは，回転方向の右旋性，左旋性によつて行われたものではなく，砂側を選択した結果であることは明らかである。

次に密度を増加していつた場合についてみる。1 個体のみの砂側の定着率は 97% であるが，更に 1 個体を追加した場合，即ち，2 個体になるとその値は 85% となり，1 個体の場合よりも，砂側へ入りにくくなつている。これは砂側の密度が高まつたので，一部の個体は，前に定着場所としての価値のより小さかつた小石側へ定着したことになり，個体相互間に反撥性のあることを示している。

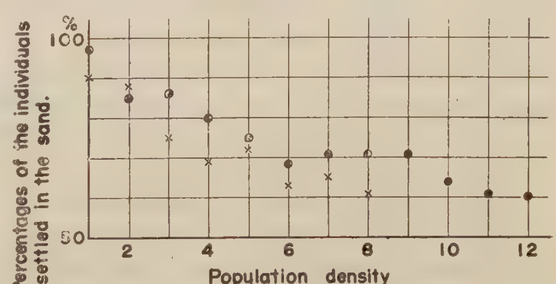


Fig 1. Mean percentages of the individuals settled in the sand ● *L. yokohamae*, × *K. bicoloratus*

更に 1 個体ずつ追加して密度の増加に伴う砂側への定着率がどのように変化するかをみるために，順次個体数を増加させ 12 個体まで行つた。その結果は Fig. 1 に示すように，全個体数に対する砂側の個体数の百分率は，密度が高くなるにしたがつて段々と 50% に近ずいてくる。即ち一つの閉鎖空間内では低密度ではより良い場所に個体が集合するが，密度の増加に伴なつて，分布が環境の不均一性にかかわらず一様化していくことがみられる。

2.　イシガレイ

マコガレイと同様なことを行つた。1 個体の場合の砂側の定着率は 90% であり，マコガレイに比較してその値は低い。又密度を増加させ 8 尾まで入れた場合の砂側への定着率の変化は Fig. 1 にみられるように

その減少の程度はマコガレイよりもイシガレイの方がより急激であり，より低い個体密度で平衡状態に達するようである。

上にのべたことは要するに，密度が増加すると砂側への定着率は減少し，その率は入れられた個体数によつて変つてくるということである。

環境密度理論の適用

これらの現象を解析するために，環境密度理論にもとずく確率式を適用してみる。森下の理論によると，はじめG（小石側）よりも好適であつたS（砂側）は，その中に何個体か定着することにより環境条件が悪化して，丁度Gの場所の悪さと釣合う程度の悪さにまで変化したと考えられる。即ち場所Gの悪さは場所Sの悪さにある棲息密度が加わつた悪さに等しいと考えられる。今S．G．2つの場所の価値を棲息密度に換算しうるとして，それぞれの値を E_S．E_g．その差を a とすると

$$a= E_S-E_g|=x$$

この場合環境条件がよいということは，E の値が低いことに相当する。ここでは $E_S<E_g$ となる。
E_S, E_g は「環境密度」と呼ばれる。

今 S に最初の個体が入る確率が G に入る確率よりも高いということは，E_S が E_g よりも小さいということであつた。S 及び G に入る確率は E_S と E_g の高さに逆比例するものと仮定すると，最初の個体が S に入る確率 $P_{1(1)}$ は，$P_{1(1)}=\frac{E_g}{E_S+E_g}$．$S$ に入らない確率は $P_{0(1)}\ \frac{E_S}{E_S+E_g}$ であり，n 個体を入れた場合 S 側における密度が E_S+x ($x=0,\ 1,\ 2,\cdots\cdots n$) である確率を $P_x(n)$ とすれば ($n+1$) 個体の場合の確率は

$$P_x(n+1)=\left(\frac{E_S+x}{E_S+E_g+n}\right)P_x(x)+\left(1-\frac{E_S+x-1}{E_S+E_g+n}\right)P_{x-1}(n)\cdots\cdots(1)$$

である。但し S の面積$=G$ の面積
上式の確率計算のためには，E_S，E_g の値を求める必要がある。
それは

$$E_g-E_S=a \qquad E_g/E_S=b$$

のときの a，b がわかればよい。
a の値は水槽中に次々と個体を入れた場合には，やがて

$$E_S+N_S=E_g+N_g \quad \text{の状態に近ずく。}$$

但し N_S，N_g は S，G 側の個体数を示す。これより

$$E_g-E_S=N_S-N_g=a$$

として a が求まり
$b=E_g/E_S$ は1個体の場合，S．G．の側に入る個体の確率の比である。

マコガレイの E_S．E_g を計算すると6個体より12個体の N_S-N_g の平均値を使用して 3.0 となり，$a=3.0$ で $b=31/1=31$ となる。

この a，b の値より $E_S\fallingdotseq0.1$，$E_g\fallingdotseq3.1$ となる。
これらの値を用いて，（1）式によつて各個体数の場合の S．G 各部分の分布確率を計算し，その確率及び分布の理論頻度と実測頻度とを比較すると第2表のようになり，理論値と観測値は，個体数 8．9 の場合にやや異なるが大体一致している。故にマコガレイの S．G 両側における分布の機構は環境密度理論に従つており，環境密度の値は 0.1，3.1 である。

イシガレイの場合も，6個体から3個体までの N_S-N_g の平均値を用い，$a=1.73$，$b=18/2=9.0$ となる。a，b の値より $E_S=0.22$，$E_g=1.95$ をえる。それぞれの個体数の場合への分布の理論頻度と実測頻度を比較すると第3表のように，両者の値はよく一致する。以上マコガレイ，イシガレイの両種に対する密度の増加に伴う棲息場所選択は，環境密度理論によつて充分説明される。

Table 2. Frequency distribution of the individuals of *L. yokohamae* settled in the sand and their expected values calculated by Morisita's formula under the various population densities

Total number of individuals	Number of individuals in the sand	Erequency	Probability	Expected value
1	1	31	0.968	30.9
	0	1	0.032	1.1
2	2	14	0.715	14.3
	1	6	0.284	5.7
	0	0	0.001	0.0
3	3	12	0.529	11.6
	2	8	0.410	8.2
	1	0	0.061	0.1
	0	0	0.000	0.0
4	4	7	0.331	6.6
	3	10	0.469	9.4
	2	3	0.189	3.8
	1	0	0.011	0.2
	0	0	0.000	0.0
5	5	4	0.204	4.0
	4	8	0.392	7.8
	3	7	0.336	6.7
	2	1	0.066	1.3
	1	0	0.002	0.2
	0	0	0.000	0.0
6	6	1	0.077	1.5
	5	6	0.323	6.4
	4	8	0.405	8.1
	3	4	0.176	3.5
	2	1	0.019	0.4
	1	0	0.000	0.0
	0	0	0.000	0.0
7	7	2	0.007	1.3
	6	4	0.195	3.9
	5	7	0.403	8.1
	4	6	0.296	5.9
	3	1	0.064	1.3
	2	0	0.005	0.1
	1	0	0.000	0.0
	0	0	0.000	0.0
8	8	1	0.042	0.8
	7	4	0.170	3.4
	6	5	0.218	4.4
	5	8	0.379	7.6
	4	1	0.163	3.3
	3	1	0.023	0.5
	2	0	0.005	0.1
	1	0	0.000	0.0
	0	0	0.000	0.0

Total number of individuals	Number of individuals in the sand	Frequency	Probability	Expected value
9	9	2	0.027	0.5
	8	2	0.090	1.7
	7	5	0.206	4.1
	6	5	0.319	6.4
	5	5	0.277	5.5
	4	1	0.081	1.6
	3	0	0.004	0.1
	2	0	0.001	0.0
	1	0	0.000	0.0
	0	0	0.000	0.0
10	10	0	0.006	0.0
	9	1	0.048	0.9
	8	3	0.142	2.8
	7	5	0.279	5.6
	6	6	0.321	6.4
	5	4	0.171	3.4
	4	1	0.030	0.6
	3	0	0.002	0.0
	2	0	0.000	0.0
	1	0	0.000	0.0
	0	0	0.000	0.0
11	11	0	0.000	0.0
	10	0	0.019	0.4
	9	2	0.087	1.7
	8	5	0.216	4.3
	7	6	0.322	6.4
	6	4	0.254	5.1
	5	2	0.087	1.7
	4	1	0.010	0.2
	3	0	0.000	0.0
	2	0	0.000	0.0
	1	0	0.000	0.0
	0	0	0.000	0.0
12	12	0	0.000	0.0
	11	0	0.000	0.0
	10	2	0.045	0.9
	9	3	0.148	3.0
	8	6	0.284	5.7
	7	6	0.306	6.1
	6	3	0.165	3.3
	5	0	0.034	0.7
	4	0	0.003	0.1
	3	0	0.000	0.0
	2	0	0.000	0.0
	1	0	0.000	0.0
	0	0	0.000	0.0

Table 3. Frequency distribution of the individuals of *Kareius bicoloratus* settled in the sand and their expected values calculated by Morisita's formula under the various population densities

Total number of individuals	Number of individuals in the sand	Frequency	Probability	Expected value
1	1	18	0.900	18.0
	0	2	0.100	2.0
2	2	15	0.554	11.1
	1	5	0.426	8.5
	0	0	0.020	0.4
3	3	8	0.259	5.2
	2	9	0.596	11.9
	1	3	0.144	2.9
	0	0	0.001	0.0
4	4	3	0.104	2.1
	3	9	0.501	10.1
	2	8	0.360	7.2
	1	0	0.035	0.7
	0	0	0.000	0.0
5	5	2	0.096	1.9
	4	8	0.310	6.2
	3	10	0.490	9.8
	2	0	0.099	2.0
	1	0	0.007	0.0
	0	0	0.000	0.0
6	6	0	0.024	0.5
	5	3	0.197	3.9
	4	10	0.453	9.1
	3	6	0.288	5.8
	2	1	0.037	0.7
	1	0	0.001	0.0
	0	0	0.000	0.0
7	7	0	0.007	0.1
	6	2	0.089	1.8
	5	8	0.345	6.9
	4	8	0.408	8.2
	3	2	0.140	2.8
	2	0	0.011	0.2
	1	0	0.000	0.0
	0	0	0.000	0.0
8	8	0	0.002	0.0
	7	1	0.034	0.7
	6	4	0.209	4.2
	5	8	0.416	8.3
	4	7	0.279	5.5
	3	6	0.057	1.1
	2	0	0.003	0.0
	1	0	0.000	0.0
	0	0	0.000	0.0

考　　　　　察

マコガレイとイシガレイの両魚種の環境密度の値を比較すると，物理的には等しい砂・小石であるが，両魚種にとつては環境の価値が異なり，砂側はマコガレイ 0.1 がイシガレイは 0.2 である。小石側はイシガレイ 1.95，マコガレイ 3.1 であり，イシガレイにとつてはマコガレイより非常に良好な場所であることがいえる。砂と小石という2つの異質環境の差は，マコガレイの方がイシガレイよりも，はるかに大きいことがわかり，この傾向は自然における分布状態と同様である。

環境密度の値は，種々の環境要素の変化—空間の大きさ，粒子組成，水温の高低，光の状態等—によつて異なることが知られている。ここでは，底質が種々の環境要素を含めて，すでに各魚種と一定の結びつきができているという前提の許に実験を行つたが，今後種々の条件下で実験を行い，自然における分布様式の機構を明らかにしたいと考える。

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Studies on Physico-Chemical Properties of Marine Products and Related Substances—I. Swelling and Elastic Behavior of Thermally Contracted Dried Cuttle-Fish

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Introduction

This series of papers is concerned with a study on physical and physico-chemical properties of marine products and substances related to fishery technology. The purpose of this study is twofold: One is to evaluate some of the physical and physico-chemical properties for given substance as correctly as possible and to correlate them with its other (for example, chemical) properties or its practical applicability, and the other is to demonstrate that the methods and techniques currently used in the study of high polymeric substances are useful for the physico-chemical investigation of substances in which fishery scientists and technologists are interested. In fact, there are a number of interesting problems in fishery technology which would be treated successfully or at least systematically if the methods of high-polymer chemistry are properly applied. As a typical example of such problems one may consider the mechanical properties of "Kamaboko."[1] (Kamaboko is a heat-coagulated fish paste containing some salt, sugar, starch and flavor; it is one of the favorites of Japanese people). Although some of its mechanical properties such as the breaking strength and elongation have been investigated in some detail because of their importance in relation to its commercial quality and its taste, there still remain a number of problems to be investigated more deeply concerning its mechanical behavior, particularly its interpretation and its relation to the chemical structure and nature of fish meats used as the raw material. It is belived that these problems will be best treated using the methods of high-polymer physical chemistry, because Kamaboko is not only a typical viscoelastic substance, well compared to ordinary rubberlike high polymeric solid, but presents itself a complex high polymeric gel (protein gel). Some of our investigations on these problems will be presented in subsequent parts of this series. It is hoped that a series of investigations presented in this series of papers stimulates and serves to apply various interesting and useful methods of high polymer physical chemistry to the study of substances related to fishery science and technology.

In Part I and II of the series, data for swelling and elastic behavior of a dried cuttle-fish ("Surume") in water, urea solutions and a $NaHSO_3$ solution are presented and discussed in terms of the theory of polymer networks.

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Experimental

The dried cuttle-fish* used as the sample for this study was purchased from a market at Amanohashidate, Kyoto Prefecture. It appeared to be of a considerably high grade from the commercial point of view. The mantle portion was cut finely in strips along the direction of its fiber axis and, after being soaked in boiling water for one hour to remove water soluble portions and impurities, the strips were shaped to a number of test specimens of dimensions $3\times1\times50$ mm. using a razor blade. They were then made dry sufficiently over phosporous pentoxide**.

The swelling measurements were carried out according to the following procedure: The dry specimen was placed in a test tube containing the medium in which the test was to be run, taken out of the tube at regular intervals and weighed carefully after wiping it gently with filter paper. This procedure was continued until the change in weight of the specimen became no longer detectable. The swelling ratio*** of the sample, q, was calculated from the weight of the sample, W, by means of the equation:

$$q=\frac{1}{v_2}=1+\frac{\rho_2}{\rho_1}\frac{W}{W_0}-\frac{\rho_2}{\rho_1}, \quad \cdots\cdots(1)$$

assuming that swelling occurs completely isotropically. † In Eq. (1), v_2 is the volume fraction of the swollen sample, W_0 is the value of W in dry state of the sample, and ρ_2 and ρ_1 are the densities of the sample in dry state and of the medium, respectively. The value of W_0 was determined, as usual, by drying the sample completely after each swelling run had been completed. The value of ρ_2 was obtained pycnometrically in benzene at 25°C. and found to be 1.290 g./cm.^{3} It should be noted that, according to HAUROWITZ,[2] there is a great experimental difficulty in the accurate evaluation of densities of dry protein samples, so that the results obtained are, in general, less reliable. The liquids used in the present work as the medium in which both swelling and elastic tests were to be done were water, water solutions of urea of different concentrations and a water solution of $NaHSO_3$ of 0.1 M concentration (pH=6). The temperature was varied from 10 to 58°C. for water, and fixed at 30°C. for the other two media. The swelling apparatus was supported in a constant temperature bath controlled carefully at a given temperature.

The apparatus employed for the stress measurements was the same as that which we had used for the study of swollen polyvinyl formal films.[3] According to the suggestion of MEYER and FERRI,[4] the stress-temperature measurements were performed as follows. First, the specimen, held at a given constant strain (elongation), was allowed to relax in water maintained at the highest of the temperatures to be studied (in the present experiments, 58°C.). When the decay of stress became negligible, the temperature of the medium was gradually lowered, keeping the specimen at the given length, and the corres-

* *Sepioteuthis lessoniana* FÈRUSSAC. We are indebted to Mr. A. OCHIAI of this Departmennt for the identification of the sample.

** The sample prepared in this manner is hereafter referred to as "thermally contracted (or denaturated) dried cuttle-fish.

*** Swollen volume divided by dry volume.

† This assumption probably does not hold for fibrous material like that treated in this work. However, no appropriate equation is yet available for this sort of material.

bonding stresses were recorded. When the lowest of the temperature range was reached, the temperature was raised at the same rate as in the cooling to check whether the heating cycle shows a hysteresis in the stress-temperature curve. The rate of cooling and heating adopted here was about 0.5°C. per minute.

Results

It was found that swelling equilibrium was attained after about 100 minutes from the start of a particular run. For completeness, the evaluation of the equilibrium swelling ratio, q_∞, was made using data obtained after 24 hours. In Table I the values of q_∞ thus obtained are listed for all the systems studied. It is seen from the table that q_∞ in water descreases with increasing temperature, indicating that the sample shrinks thermally in water. Values of q_∞ in urea solutions are higher than that in water compared at the equal temperature and increase with increasing urea concentration. For $NaHSO_3$ no significant change is observed in q_∞, again compared with that in water at the same temperature.

Table I. Epuilibrium swelling data on a thermally contracted dried cuttle-fish

Medium	Temp. (°C.)	q_∞
Water	10	5.020
〃	30	4.340
〃	45	3.795
〃	58	2.896
0.5 M urea	30	5.010
1 〃	〃	5.548
2 〃	〃	(5.610)
5 〃	〃	7.940
0.1 M $NaHSO_3$ (pH6)	〃	4.156

With the technique described in the previous section, it is only possible to determine the stress-temperature relation at a fixed length of the sample, because the sample changes its original length (length at load-free state) with temperature as found from Table I. The strees-temperature curve thus obtained cannot be regarded as the stress-temperature curve at a fixed strain, although at the highest temperature (58°C. in the present experiments) used in such experiments, the measured stress corresponds exactly to the given strain. However, it is possible to derive the required stress-temperature curve at a fixed strain from a family of such stress-temperature data obtained at several fixed lengths of the sample. In this derivation, it is also necessary to know the original length of the sample as a function of temperature over the range in question. This information can be obtained, to a first approximation from the corresponding equilibrium swelling data (Table I) if we assume simply that swelling occurs isotropically. The method for deriving the required stress-temperature curve at a given strain on the basis of these data is described in reference (5). Here we give only the results obtained by applying this method to our experimental data. Figure 1 shows those results graphically, where stress f (dynes/cm.^{2}) is plotted against temperature at several different strains. It is seen from this figure

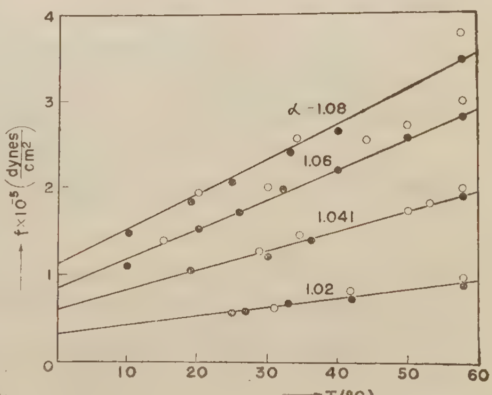


Fig. 1. Stress-temperature relations for thermally contracted dried cuttle-fish swollen in water at different extension ratios. ●: decreasing temperature; ○: increasing temperature

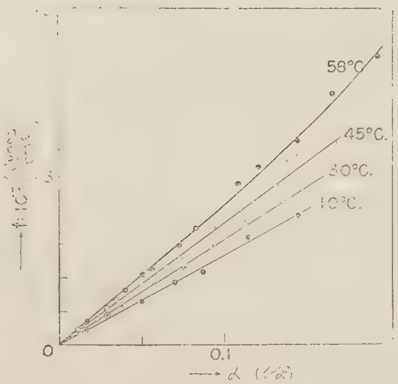


Fig. 2. Modified stress strain curves for thermally denaturated dried cuttle-fish swollen in water at different temperature

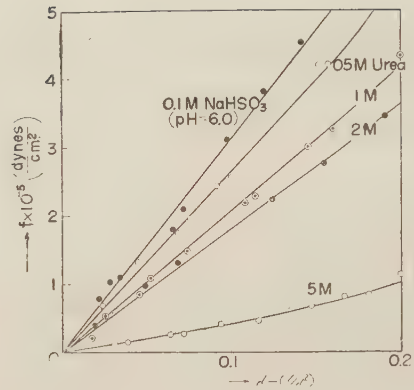


Fig. 3. Modified stress-strain curves for thermally denaturated dried cuttle-fish swollen in urea solutions of different concentrations and in 0.1M $NaHSO_3$ solution at 30°C

that all the plotted curves are linear over the whole temperature range indicated and that the temperature cycle does not show any significant hysteresis in all cases studied. It is interesting to note that the slopes of these straight lines are positive, just as is the case with vulcanized rubber[6] and GR-S synthetic rubber,[7] in spite of the apparently fibrous structure of the cuttle-fish tissue. It is known that the slopes of stress-temperature curves for fiberlike materials are usually negative.[8]

Figure 2 shows the stress-strain curves of the sample in water at different temperatures. In Figure 3 the corresponding curves in urea and $NaHSO_3$ solutions are given. In both figures, the stress is plotted against the function $\alpha-(1/\alpha^2)$, where α is the extension ratio (stretched length divided by original length), in accordance with the kinetic theory of rubberlike elasticity.[6] It should be mentioned that the limiting slope at the origin of this relation yields the elastic modulus of the sample. By comparison of Figures 2 and 3 it is found that the elastic modulus in 5 M urea solution is as small as one tenths the value in water at the same temperature. This means definitely that urea acts very effectively to make the structural network of the cuttle-fish tissue loosen. In contrast, no significant change of this kind can be obtained with $NaHSO_3$, in exact conformity to the corresponding information from the swelling measurement for this system described above.

A discussion of the experimental results presented here will be made in Part II in terms of the current theory of polymer networks.

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Studies on Physico-Chemical Properties of Marine Products and Related Substances—II. Analysis of Elastic Behavior of Thermally Contracted Dried Cuttle-Fish

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This paper is concerned with a theoretical interpretation of the experimental results presented in Part I on the basis of the theory of polymer networks.

Theoretical Equations

Before proceeding to the analysis of experimental data, a brief description is given of the theoretical equations in terms of which the analysis is to be made.

Based on the principles of thermodynamics[1], the tensile stress required to stretch a solid composed of a single component in the absence of flow may be given as the sum of two terms:

$$f=\left(\frac{\partial E}{\partial l}\right)_{T,V}-T\left(\frac{\partial S}{\partial l}\right)_{T,V}, \qquad (1)$$

where f is the retractive force per unit area (i.e., stress), $(\partial E/\partial l)_{T,V}$ is the change of internal energy E with length l at constant temperature T and volume V, $(\partial S/\partial l)_{T,V}$ is the change of entropy S with length at constant temperature and volume, and T is the absolute temperature. Thus, if one writes

$$f=f_E+f_S, \qquad (2)$$

with

$$f_E=(\partial E/\partial l)_{T,V} \text{ and } f_S=-T(\partial S/\partial l)_{T,V}, \qquad (3)$$

f_E is the force arising from an energy mechanism and f_S is that from an entropy mechanism. Since, according to thermodynamics,

$$(\partial S/\partial l)_{T,V} \cong -(\partial f/\partial T)_{\alpha,P} \qquad (4)$$

where α is the extension ratio, f_S can be put in the form:

$$f_S=T(\partial f/\partial T)_{\alpha,P} \qquad (5)$$

It is thus possible to evaluate the entropy force component f_S from stress-temperature data obtained at fixed values of α and P. Besides the dependence on pressure which is generally negligible under ordinary experimental conditions, f_S may depend on both α and T. The energy force f_E is then calculated as functions of α and T from known data of f (α, T) using Eq. (2).

KATZ[2] has extended thermodynamic treatments to include two-component systems. The work described in Part I was carried out with the two-component systems: dried

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cuttle-fish—water, —urea solution, and—$NaHSO_3$ solution; however, because of the lack of experimental data needed for this refinement, use is not made in this paper of KATZ's equations, and the analysis below will be made in terms of Eqs. (2), (3) and (5). Such an approximate treatment was also adopted by BRYANT and WAKEHAM[3] in their stress-temperature study on cellulose fibers in water.

Equation (1) is a general statement and applies to all materials composed of a single component. In the case of rubbery polymeric materials which show negligible flow, f_E is small, and in the extreme of "ideal" rubbers, it is assumed to vanish. For such materials

$$f=f_S=-T(\partial S/\partial l)_{T,V}\ , \qquad (6)$$

According to the current theory of high polymer networks, it is stated that when a polymer network having negligible energy force component is made swell in a liquld, Eq. (6) takes the form:

$$f=\frac{RT\rho_2(v_2)^{1/3}}{M_C}\left(\alpha-\frac{1}{\alpha^2}\right), \qquad (7)$$

where M_C is the average molecular weight of the polymer chain between network junction points (commonly referred to as "points of crosslinking"). For the lack of space allowed we here do not go into the physical picture of such a polymer network as described by Eq. (7), details of which are given in references (4) and (5). Equation (7) shows that at a fixed temperature and swelling ratio stress f should vary linearly with $\alpha-(1/\alpha^2)$. However, it is important to note that this linearity is not always the absolute criterion for the fact that the polymer in question has a negligible energy effect. In fact, it is demonstrated below that, while, in all systems examined in Part I, f varies quite linearly with $\alpha-(1/\alpha^2)$ within the limits of small strains, the energy contribution to f is considerable even at such degrees of stretching. This situation makes the application of Eq. (7) to our data impractical; however, use will be made of this equation to obtain some rough idea for the magnitude of M_C in the systems studied here.

Analysis of Data

The data presented in Figure 1 of Part I of this series will now be analyzed by means of Eq. (5) to obtain f_S as functions of α and T. Values of f_E are then calculated, using again the same data combined with the values of f_S obtained. By way of example, the values of f_S and f_E thus obtained for 50°C. are plotted against α in Figure 1, where the corresponding f values are also shown. It is seen from the figure that over the range of extension ratio indicated, f_S is positive and f_E is negative. The fact that f_S takes increasing positive values

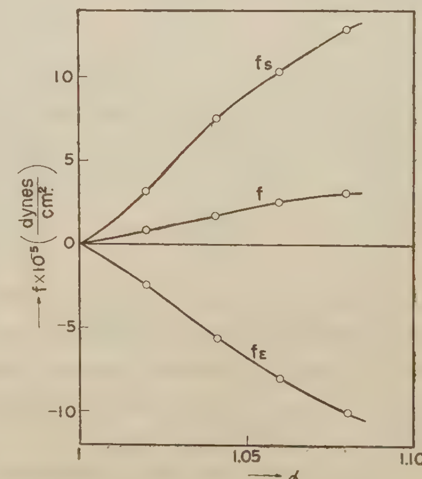


Fig. 1. Total stress and stress components for thermally contracted dried cuttle-fish swollen in water at 50°C. plotted against extension ratio

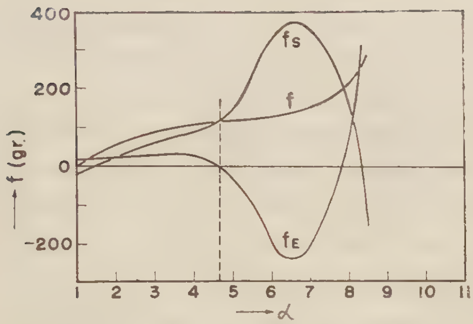


Fig. 2. Total force and force compenents for natural rubber (from GUTH[7])

with α indicates that the chain molecules consisting the tissue of dried cuttle-fish tend to assume less random configuration upon stretching, i.e., the material becomes more ordered with stretching. The large negative energy effect as observed here is an indicative of that interchain energy bonds are increased cooperatively as the chains are straightened out upon stretching. Formation of such bonds decreases the internal energy of the system and effectively aids in extending the sample strip. It is supposed that in the present system hydrogen bonds are certainly responsible for this effect to a large extent. It is interesting to note that similar large negative energy effects have been observed for casein, nylon and others[6]. It is also instructive to compare the present results with those for natural rubber obtained by GUTH[7] (Figure 2). It is noted from this figure that our data on a dried cuttle-fish swollen in water are closely similar in behavior to those on natual rubber at high extensions. GUTH has attributed a large negative energy effect in natural rubber at high extensions to the crystallization of rubber molecules. If an analogy consideration is permitted, it may be supposed that the chain molecules of dried cuttle-fish tissue are in a fairly extended form even at small extensions, which, in turn, favors to get a considerable energy effect produced at low extensions.

Since it was demonstrated that the energy contribution to f is not negligible in the present system, use of Eq. (7) to our data is apparently impractical; however, some approximate estimate of the magnitude of M_C may be obtained by fitting Eq. (7) to the data given in Figures 2 and 3 of Part I, where, in all cases indicated, f varies linearly with $\alpha-(1/\alpha^2)$ within the limits of small extensions, in agreement with Eq. (7). Values of M_C thus obtained are recorded in Table I. It is seen from the table that M_C in water is practically independent of temperature within the limits of experimental error, while M_C in urea solution increases markedly with increasing urea concentration.

Table I. Average molecular weights between crosslinks

Medium	Temp. (°C.)	M_C
Water	10	6500
〃	30	6100
〃	45	5900
〃	58	6000
0.5 M urea	30	7000
1 〃	〃	8800
2 〃	〃	(10000)
5 〃	〃	38000
0.1 M $NaHSO_3$ (pH=6)	〃	6600

In view of the well-known fact that urea breaks very effectively hydrogen bonding, it may well be concluded that the crosslinks responsible for elastic behavior of dried cuttle-fish in liquid medium is due at least partly to hydrogen bonding. This view is essentially different from that concluded by WIEDERHORN and REARDON[8] for the structure of themally contracted kangaroo tail collagen from a similar work as described here. The value of M_C in 0.1M $NaHSO_3$ solution is substantially the same as that in water, indicating no significant effect of this reagent on bond

breaking in the present system. It is generally accepted that $NaHSO_3$ acts to break the disulfide bond due to cystine. So the idea that the cuttle-fish tissue is crosslinked with disulfide bonds is hardly probable. This is contrasted to the case of wool keratin in which interchain crosslinkings are mainly due to disulfide bonds and hydrogen bonds.

In this work, media which are effective to break salt links were not treated. A further investigation with such media is certainly desirable, because, as pointed by TAKAHASHI[9] from stress-strain measurements on thermally contracted (raw) cuttle-fish, salt links should play an important role in the bonding pattern of cuttle-fish protein molecules.

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Studies on Physico-Chemical Properties of Marine Products and Related Substances—III. Stress-Relaxation in Dried Cuttle-Fish in Liquid Media

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Introduction

In Part II of this series it was inferred, by analyzing stress-strain data reported in Part I in terms of the theory of swollen polymer networks, that the crosslinks responsible for the elastic behavior of swollen tissues of thermally contracted dried cuttle-fish are probably due primarily to hydrogen bonds and "salt-bridges." To obtain more information about this problem, stress-relaxation measurements were carried out on water-swollen dried cuttle-fish in the presence of stress-reducing reagents. Although the results obtained are of a preliminary nature, they are reported briefly in this paper.

The stress-relaxation technique used in this work is the one usually referred to as the "chemical relaxation method." It is generally assumed, in applying this method to a system, that the decay of stress in the material held at constant strain is controlled predominantly by the chemical process such as scission of crosslinks brought about by chemical action, any physical process such as molecular rearrangement being assumed to occur much more rapidly. It is then possible, from stress-relaxation measurements, to obtain information of what chemical bonds are associated with the mechanical response of the system to a given external excitation. Thus KUBU *et al.*[1-3] worked out extensive chemical relaxation measurements of wool keratin in the presence of various reagents which are specific for the crosslinks involved in this material, and elucidated thereby the natures and rates of the chemical reactions brought about by those reagents in the system. An excellent review of the method and techniques of the chemical relaxation study is given in one of their papers[1].

The present paper is concerned with an application of this method to the study of a water-swollen thermally denaturated dried cuttle-fish, especially of the stress-supporting crosslinks involved.

Experimental

The apparatus employed for the stress-relaxation measurements in this work was the same as that described elsewhere[4]. All the measurements were done at 10°C. The samples used were obtained from the same stock as prepared in the work reported in

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Part I. The test specimen was first allowed to swell in water at 10°C. for 24 hours. It was assumed from the results reported in Part I that this interval of time had been sufficient to get the test specimen attained to swelling equilibrium in water. The specimen was then stretched quickly by a predetermind amount (3 % strain in all cases studied) and fixed at that strain. The stress thus produced was allowed to decay until the rate of relaxation became sufficiently slow. Then the water was siphoned off from the reaction chamber, and a solution of the reagent whose action to the sample was to be studied was quickly introduced. The subsequent change of stress was then recorded as before. After each run had been completed, the specimen was removed, and the chamber was rinsed thoroughly with distilled water. For comparison with these data for dried cuttle-fish similar chemical relaxation measurements were run for 250 d. multifilament yarns of Amilan (Toyo Rayon Co., 6-Nylon). The strain value used in this case was 0.5 %. The stress-reducing reagents used both for dried cuttle-fish and Amilan were 2.5 M urea, 0.2 M sodium bisulfite and 0.1 M hydrochloric acid. The urea, sodium bisulfite and hydrochloric acid were adopted, respectively, for scission of hydrogen bonds, disulfide bonds and salt-bridges. These reagents used were of C. P. grade, not purified further.

Results and Discussion

Figure 1 shows the results of stress relaxation measurements for samples preswollen in water. Here the stress f divided by its value f_0 at 0.1 min. is plotted against the logarithm of time t (in minutes). The arrow indicates the time of addition of a particular reagent. Each stress-relaxation curve was obtained using a different sample taken from the same stock; however, it is seen from Figure 1 that the results obtained show a good reproducibility when the relative force, f/f_0, is used for their representation. The stress-relaxation behavior for periods before respective reagents were added (i.e., behavior in pure water) will not be considered further in this paper, because it should form the subject of a separate article. It is observed from Figure 1 that the stress decay produced by the addition of either 2.5 M urea or 0.1 M HCl is quite appreciable and occurs very rapidly. It appears that the stress goes to zero after a certain interval of time, in either of these cases. With 0.2 M $NaHSO_3$ the stress drops somewhat less rapidly and appears to level off a certain finite amount. To know in more detail the stress decay after the time of addition of the reagent, a plot shown in Figure 2 was made, where the ratio, Ψ, of the force at time t to the force at the time of addition of the reagent is plotted against the logarithm of time. Zero time is taken at the time of addition of each reagent.

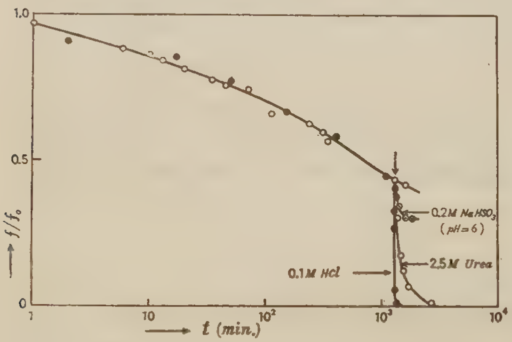


Fig. 1. Stress-relaxation of water-swollen dried cuttle- fish under the action of various chemical reagent at 10 °C. and 3 % elongation. Relative force is plotted against time on a logarithmic scale

Figure 2 demonstrates clearly the extents and relative rates of stress decay prod-

uced by the addition of various reagents. It is seen that, while either 2.5 M urea or 0.1 M HCl causes the stress to relax completely after a certain finite period, the latter is much more effective for this process than the former. The average rate of stress decay with the latter reagent is roughly 100 times that with the former. With 0.2 M $NaHSO_3$ there is an initial portion where no stress decay occurs, and which is followed by a slow and levelling-off relaxation of stress; the limiting stress is about 0.7 of the initial value.

The marked stress-reduction with 2.5 M urea as observed here is probably accounted for by the scission of hydrogen bonds, in agreement with the fact that the average molecular weight between junction points of the water-swollen dried cuttle-fish network is increased appreciabley with the addition of urea. A possible explanation of the behavior with 0.1 M HCl is that acid-sensitive bonds (possibly salt-bridges) are broken by this strong acid. Another cause of the behavior may be attributed to the increased degree of swelling of the sample in a lower pH solution. In connection with this, it may be of interest to note that when the sample subjected to the acid experiment was rinsed thoroughly and placed in pure water, the stress did not return to the original value. Contrary to this, KUBU *et al.*[1] observed a complete reversibility with wool keratin under the similar conditions as adopted here for thermally contracted dried cuttle-fish. Thus our tentative interpretation of the behavior as observed here with 0.1 M HCl is that the peptide chains of the dried cuttle-fish tissue must be broken by as dilute a HCl solution as 0.1 M. It would, of course, be too simple to attribute the observed behavior solely to the scission of the back-bone chains, and to neglect scissions of interchain crosslinks, such as hydrogen bonds and salt-bridges, which must occur concomitantly with the main chain scission. To obtain more definite information on this problem, experiments with various neutral salt solutions and under various pH conditions have to be undertaken.

Finally, similar data obtained on Amilan and wool keratin are shown for comparison, which are graphically given in Figure 3. The data on wool were taken from KUBU's paper[1]. It is seen from this

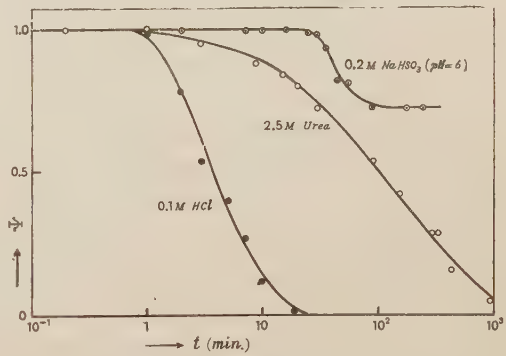


Fig. 2. Stress-relaxation of water-swollen dried cuttle-fish under the action of various reagents. The ratio, Ψ, of the force at time to the force at the time of addition of the reagent is plotted against time on a logarithmic scale

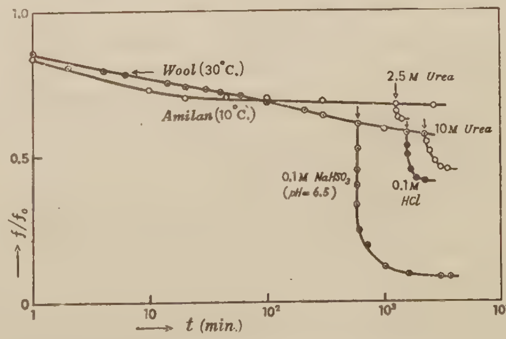


Fig. 3. Stress-relaxation of wool at 30°C. and 15% elongation (from KUBU[1]) and of Amilan at 10°C. and 0.5% elongation under the action of various reagents

figure that for wool the stress-reduction power is in order of 0.1 M $NaHSO_3$, 0.1 M HCl, and 10 M urea, while for Amilan only 2.5 M urea shows a measurable effect and the other two reagents have a negligible influence on stress relaxation. These results indicate that the disulfide bond due to cystine forms the main stresssupporting crosslinks of wool keratin, while in Amilan the hydrogen bonding plays a controlling role in its bonding pattern. These are all in good agreement with information from other sources of experimental evidence[2)5)]. That the stress-reduction of Amilan in 2.5 M urea is relatively small is safely ascribed to the crystalline structure of this polymer.

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Studies on Physico-Chemical Properties of Marine Products and Related Substances—IV. Application of RIVLIN's Method to the Rupture of Kamaboko*

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Introduction

The rupture properties of Kamaboko, such as the breaking strength and the breaking elongation, are considered as one of the most important factors in evaluating the commercial quality of this marine product. It is apparent, therefore, that detailed information about the rupture behavior of Kamaboko is of great importance from the practical point of view. Kamaboko manufacturers used to estimate the quality of their products in terms of an empirical quantity usually called "Ashi."[1] SHIMIZU and SIMIDU[2)3)] have recently shown that this quantity "Ashi" is closely related to the elastic energy stored in a given test specimen of Kamaboko before breaking. Their method is merely a modification of the method employed usually for rupture experiments of metallic materials and, therefore, is not very suitable for soft and rather highly elastic materials like Kamaboko. It is also important to note the fact that Kamaboko is not strictly uniform in the physical sense but often contains pores of various sizes originated unavoidably from its commercial processing. It is not difficult to suppose that these factors may lead to a statistical scattering of the rupture energies evaluated for Kamaboko by the use of the test method as employed by SHIMIZU and SIMIDU.

Recently RIVLIN and THOMAS[4] presented an ingenious theory for treating the rupture phenomenon of vulcanized rubber and showed that an energy for tearing, characteristic of a given material and independent of its shape, could be evaluated experimentally on the basis of this theory. Their theory assumes only the condition that the given material behaves perfectly elastically. Small pores and irregularities contained in the material are not serious in evaluating the rupture energy in terms of their method. This latter condition implies that the theory of RIVLIN and THOMAS is advantageous for the study of rupture on a material like Kamaboko. In addition, Kamaboko behaves, to a first approximation, as a perfectly elastic substance. It is of interest, therefore, to apply RIVLIN's method to the study of rupture phenomena in Kamaboko, with a particular concern to elucidate the scientific significance of the manufacturer's terminology "Ashi." This paper describes some of our preliminary studies made on the basis of this idea.

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* Part I of a series of papers on Rheology of Kamaboko.

Theory of RIVLIN and THOMAS

Before presenting the experimental data obtained, a brief account of the theory of RIVLIN and THOMAS is given. The reader should refer to their original paper[4] as for the details of the theory and the experimental method. When a thin plate of an elastic material is stretched slowly (ideally, quasistatically) in the direction of its length, the work done on the specimen is stored as the elastic energy. If the plate was given a cut (or slit) in the direction perpendicular to its edge as illustrated schematically in Fig. 1, the cut gets longer gradually with stretching of the plate. The energy stored elastically in the plate is decreased and just balanced by the increase of a certain kind of energy needed for getting the cut longer. The change in this energy is assumed to be proportional to the increase of the cut length. Since the stress in the sample is apparently concentrated in a region adjacent to the tip of the cut, this portion would be subjected to a particularly large deformation in comparison with the other part in the sample. Accordingly, almost all of the energy applied externally is stored in this portion. When the stored energy has reached a certain critical value, the cut length is increased suddenly and the rupture of the plate occurs. It is apparent from these considerations that the amount of stored energy is dependent almost entirely upon the mechanical state around the tip of the cut, and neither does upon the overall shape of the sample nor upon what test method is used. It is also apparent that small pores and other irregularities involved in the sample have little influence upon the energy concerned. RIVLIN and THOMAS formulated this idea and obtained an equation of the form:

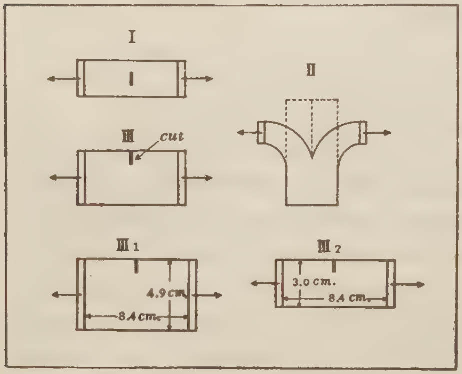


Fig. 1. Shapes and dimensions of test specimens I, II and III: used by RIVLIN and THOMAS for vulcanized rubber; III_1 and III_2: used in the present work for Kamaboko

$$-(\partial W/\partial C)_{l^*}=Tt, \quad \cdots\cdots (1)$$

where W is the elastically stored energy, C is initial cut length and t is the thickness of the sample. T represents the energy which RIVLIN and THOMAS called the characteristic energy for tearing. According to their theory, T should be characteristic of the given material, independent of its shape, method of test, and others. The subscript l^* indicates the condition that the differentiation should be performed at such a specific rupture elongation as independent of the initial cut length.

Experimental and Results

Three species of Kamaboko were purchased at a market in Maizuru. They were regarded as of high, medium and low grades according to their prices, and were designated as A, B, and C, respectively. These products were cut into thin plates of about 0.15 cm. thickness using a meat-slicer. A cut of desired length C was given to each of the

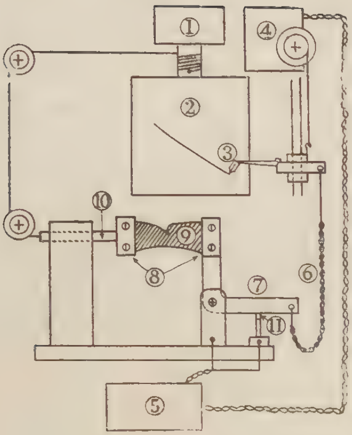


Fig. 2. Schematic diagram of the apparatus used. ① motor synchronized with a clock. ② recording drum. ③ pen. ④ driving unit. ⑤ electronic relag. ⑥ chains. ⑦ Angle-shaped beam. ⑧ clamps. ⑨ test specimen. ⑩ guiding rod. ⑪ point of electric contact

plates in the pattern as type Ⅲ illustrated in Fig. 1. Most experiments were made with the plates of dimensions shown as type III_1. The sample plate was clamped in an automatic tension-meter equipped with a stress-recorder, and stretched at a constant rate of elongation (0.33 mm./sec.). The change in length of the cut upon stretching was observed through a low-power microscope. A schematic diagram of the apparatus used is presented in Fig. 2, along with brief descriptions of its important parts. The essential mechanism of this apparatus is based on the principle of the chainomatic balance which has recently been used in the Laboratory with considerable success for the study of stress-relaxation on high polymeric solids.[5] The force vs. elongation curve is recorded automatically on the rotating drum, as schematically shown in Fig. 2. The stretching can be stopped off electically just at the instant when the catastrophic rupture of the sample has occurred.

A series of force vs. elongation curves obtained

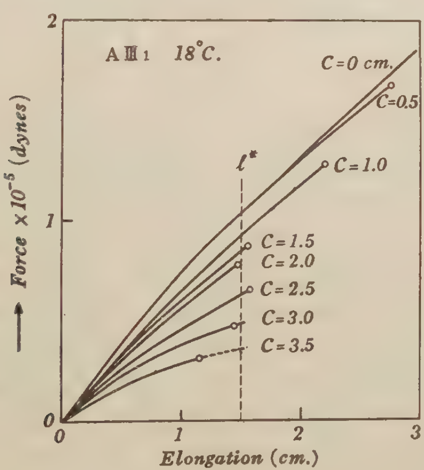


Fig. 3. Typical force vs. elongation curves for sample A; C denotes the initial cut length

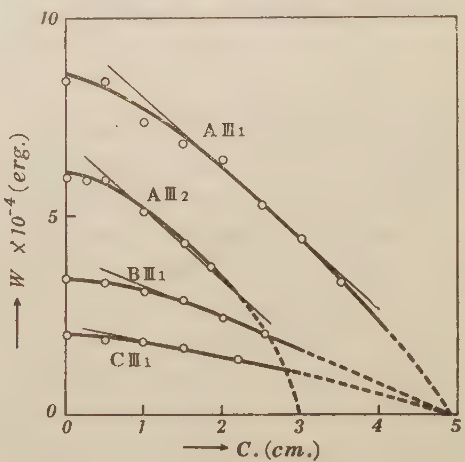


Fig. 4. W vs. C curves for samples A, B and C; The thin solid lines represent the slopes from which the respective T values have been determined

for different values of cut length C is shown in Fig. 3, where the open circles indicate the points at which the ruptures occurred. It is seen from the figure that, although the rupture elongations are dependent on the initial cut length, there exists a region in which the rupture elongations are practically independent of C. The existence of such a specific region of C is the essential condition in use of RIVLIN's theory for practical system. The specific rupture elongation, l^*, appearing in Eq. (1) may then be determined by averaging such rupture elongations as practically independent of C. This procedure for determining

l^* is illustrated graphically in Fig. 3. The area enclosed by the force vs. elongation curve, the abscissa and the vertical line through the elongation corresponding to l^* yields the value of W in Eq. (1). The values so obtained for W are plotted against C in Fig. 4. The curves, $AIII_1$, $BIII_1$ and $CIII_1$, were obtained with samples of dimensions type III_1 in Fig. 1 and the curve $AIII_2$ was with sample A of dimensiens type III_2. The data on the sample of the latter type were obtained to examine the effect of sample dimensions on the value of T. All curves in Fig. 4 are not exactly linear, as was the case with vulcanized rubber studied by RIVLIN and THOMAS.[4] However, as indicated in the graph by thin solid lines, there are regions of C in which W decreases approximately linearly with increasing C. The application of Eq. (1) to these linear portions yields the following figures for T of samples A, B and C:

Sample	T (erg. cm.$^{-2}$)
A	1.2×10^5
B	0.5×10^5
C	0.3×10^5

No significant difference is noted between T values from the curves $AIII_1$ and $AIII_2$. This implies that the value of T is independent of the dimensions of the test specimen. RIVLIN and THOMAS showed on vulcanized rubber that the value of T derived from different test methods agreed well within the practical accuracy. The methods they used to tear the rubber specimen are illustrated as I, II and III in Fig. 1.

Discussion

First it is worthwhile to note that the values of T for three samples A, B, and C exactly in order of their commecial prices. This indicates that the characteristic energy for tearing T, as introduced by RIVLIN and THOMAS is a useful measure also for the evaluation of the commerical quality of Kamaboko. There then arises a question: What relation exists between the quantity T and the Kamaboko manufacturer's terminology "Ashi"? The concept "Ashi" involves to a great extent a psychological element which cannot be defined in terms of scientific quantities. It must essentially be a complex of human reactions to the rheological behavior of Kamaboko. Thus it seems that the relation of the rheological properties of Kamaboko, such as the tearing energy T as discussed above and the breaking energy as studied by SHIMIZU and SIMIDU,[3] to "Ashi" need be considered primarily from the so-called psycho-rheological point of view.[6]

It is the common sense that the rupture phenomenon is essentially of a statistical nature, so that data on any rupture experiment would not be complete unless they were subjected to an appropriate statistical analysis. In the present work, in order to examine this point, the tearing experiments were repeated 11 times for sample A of type III_1 with the same cut length of 2 cm. The rupture elongations obtained were scattered considerably. The standard deviation from the mean rupture elongation was found to be 0.1. It is believed that this value of the standard deviation is much smaller than those of usual rupture data on Kamaboko.

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Studies on Physico-Chemical Properties of Marine Products and Related Substances—V. Heat Conductivity of Fresh Fish Meats

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Introduction

The study of heat conduction in fish meats is of practical importance in connection with the heat sterilization of canned fish. Although many investigations have been made of this problem both theoretically and experimentally, almost all existing theories neglect the change in physico-chemical properties of fish muscle caused upon heating[1]. In a previous paper[2], FUJITA presented an approximate theory for dealing with the conduction of heat in fish meat packed in a flat can under the assumption that heating of a fresh fish muscle gives rise to a change in its heat conductivity, and applied it to a hypothetical case in which the heat conductivity increases with temperature following a sigmoidal curve. This sigmoidal temperature dependence of the heat conduction was presumed on the basis of the fact that fish meats usually coagulate thermally in th range 45 to 70°C. and maintain distinctly different states below and above this temperature region.

The purpose of the present paper is to describe an approximate method for determining the temperature dependence of the heat conductivity of a given fish meat from data obtained with the sample packed in a flat can and to illustrate it in terms of some preliminary experiments on mackerel.

Method

Consider the conduction of heat in a fish meat packed in a flat can of thickness $2X$ which is immersed in a liquid kept at constant temperature θ_e. If the heat flow occurs only in the direction of the thickness of the can, the temperature θ at time t and position x in the can is governed by the unidimensional heat conduction equation:

$$C\rho \frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x}\left[k(\theta)\frac{\partial \theta}{\partial x}\right], \qquad (1)$$

where the space variable x is taken in the direction of heat flow, and $k(\theta)$, C and ρ are the heat conductivity, the specific heat and the density of the meat, respectively. In the present treatment, $k(\theta)$ is considered as a function of θ only, and both C and ρ are assumed to be constant. Taking the origin of the x-axis at the center of the can, the boundary and initial conditions for θ are

$$\theta = \theta_e \quad (x = \pm X,\ t > 0), \qquad (2)$$

$$\theta = \theta_0 \quad (-X < x < X,\ t = 0). \qquad (3)$$

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Here it has been assumed that initially the meat is maintained at uniform temperature θ_0.

No analytic solution of Eq. (1) subject to conditions (2) and (3) is yet known for the case in which k varies with θ. For this reason, we shall, in what follows, adopt an approximate procedure which may be useful for k dependent not very strongly on temperature. This consists of replacing $k(\theta)$ by an average heat conductivity, $\bar{k}$, defined by

$$\bar{k}=(\theta_e-\theta_0)^{-1}\int_{\theta_0}^{\theta_e}k(\theta)d\theta. \quad\cdots\cdots(4)$$

Equation (1) with constant heat conductivity $\bar{k}$ can be solved under conditions (2) and (3) (See, for example, reference 3), giving for the temperature at the center of the can, θ_c, the equation:

$$\frac{\theta_c-\theta_0}{\theta_e-\theta_0}=1-\frac{4}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{(2n+1)}\exp\left[-\frac{(2n+1)^2\pi^2\bar{k}t}{4C\rho X^2}\right]. \quad\cdots\cdots(5)$$

For large enough t this is satisfactorily approximated by

$$\frac{\theta_c-\theta_0}{\theta_e-\theta_0}=1-\frac{4}{\pi}\exp\left(-\frac{\pi^2\bar{k}t}{4C\rho X^2}\right), \quad\cdots\cdots(6)$$

from which one obtains

$$-\ln(\theta_e-\theta_c)=-\ln\frac{4}{\pi}(\theta_e-\theta_0)+\frac{\pi^2\bar{k}t}{4C\rho X^2}. \quad\cdots\cdots(7)$$

Thus it may be expected that a plot of $-\ln(\theta_e-\theta_c)$ against t becomes linear for large t and that the slope of this straight line permits the evaluation of $\bar{k}$ with known values of C, ρ and X. In general, the value of $\bar{k}$ thus obtained depends both on θ_e and θ_0.

Since Eq. (4) can be written

$$(\theta_e-\theta_0)\bar{k}=-\int_{\theta_r}^{\theta_0}k(\theta)d\theta+\int_{\theta_r}^{\theta_e}k(\theta)d\theta \quad\cdots\cdots(8)$$

with θ_r being chosen arbitrarily, plots of $(\theta_e-\theta_0)\bar{k}$ against θ_e for different initial temperatures θ_0 should be different, in the direction of the ordinate axis, by constant amounts given by

$$-\int_{\theta_r}^{\theta_0}k(\theta)d\theta$$

from that obtained with θ_r as θ_0. This means that the plots for different θ_0 values can be made superpose by shifting them vertically by proper amounts to form a single composite curve. It is obvious that the composite curve thus formed is no more than the $(\theta_e-\theta_0)\bar{k}$ vs. θ_e plot which would be obtained at $\theta_0=\theta_r$. For convenience, this composite curve is referred to as the **master intergral heat conductivity curve** at **reference temperature** θ_r. Since the first integral in Eq. (8) vanishes for $\theta_0=\theta_r$, the equation for the master integral heat conductvity curve, denoted by $P(\theta_e)$, is given by

$$P(\theta_e)=\int_{\theta_r}^{\theta_e}k(\theta)d\theta. \quad\cdots\cdots(9)$$

It follows then that

$$k(\theta_e)=\frac{d}{d\theta_e}P(\theta_e) \quad\cdots\cdots(10)$$

Thus the problem of determining the heat conductivity, k, as a function of temperature

is reduced to constructing the master intergral heat conductivity curve at a suitably chosen reference temperature according to the procedure described above.

Results and Discussion

The flat can used was a copper-made cylinder, 6 cm. in diameter and 2.5 cm. in thickness. To keep the heat flow in the can unidimensional in the direction of its thickness, its cylindrical surface portion was thermally insulated by covering it with thick layers of asbesto. A thin thermometer, inserted through the cylindrical surface portion so as to keep the bulb just at the center of the can, was used to measure θ_c. After the sample meat had been packed in, the can was allowed to stand for one hour in air kept at the desired initial temperature θ_0. The can was then quickly transferred into a water-bath kept at the desired external temperature θ_e, and the subsequent change of θ_c was measured as a function of time. The water-bath was vigorously stirred so that the the surface temperature of the can could be maintained equal to the external temperature during a particular run.

The specific heat of the contents was assumed to be equal to that of water at 15°C. for all the samples studied. The density of each sample was calculated from its known weight and volume.

The sample fish studied in this work was mackerel purchased at a market in Maizuru. On every series of measurements fresh fish were purchased and used immediately to make the experimental results free of any effect brought about by their natural denaturation. Only muscle portions were cut out of the sample fish and, after mincing them thoroughly, packed tightly in the can.

Figure 1 shows typical experimental data on $-\ln(\theta_e-\theta_c)$ vs. t obtained for various values of θ_e with a fixed θ_0 of 29.0°C. It is seen that all the plotted curves are satisfactorily linear over a wide range of time, in agreement with Eq. (7). Such linear relations were found in all cases studied in the present work. From the slopes of these straight lines the values of k were computed as a function of θ_e for each θ_0 studied. The values of $(\theta_e-\theta_0)\,k$ were then plotted against θ_e with θ_0 as parameter. It was found that the resultant curves could be reduced satisfactorily to a single curve (i.e., the master integral heat conductivity curve) by shifting them properly along vertical axis. The solid line in Figure 2 shows the master curve thus obtained, where the reference temperature has been chosen as 21.6°C. For comparison, data were obtained also on a mackerel sample to which 5 % soya-bean oil had been added, and are plotted in Figure 2 by dashed line.

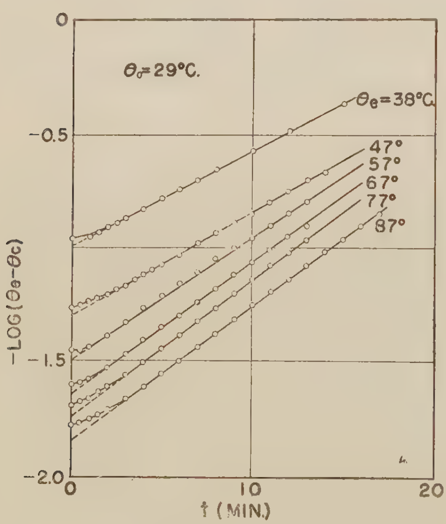


Fig. 1. Temperatures of the center of the can, θ_c, plotted semi-logarithmically aganst time t (min.) for various values of ihe external temperature, θ_e, at a fixde tvalue of the initial temperature, θ_0

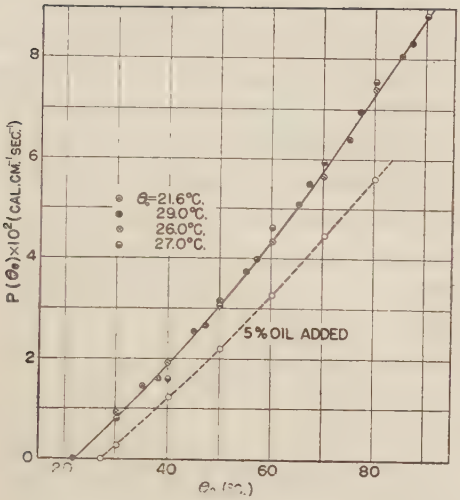


Fig. 2. The master intergral heat conductivity curve reduced to reference temperature $\theta_r=21.6°C.$; $P(\theta_e)$ is actually $\bar{k}$, (mean heat conductivity between tempetures of θ_e and θ_0) multiplied by $\theta_e-\theta_0$

By differentiating graphically these curves in Figure 2, the curves shown in Figure 3 are

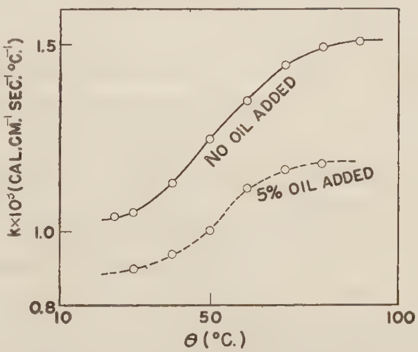


Fig. 3. Temperature dependence of the heat conductivity k for mackerel. Solid line represents the data for mackerel containing no added oil, and dashed line the data for the mackerel containing 5% added soya-bean oil

obtained, which give the heat conductivity as a function of temperature for mackerel containing no added oil (solid line) and for the one containing 5% added oil (dashed line). It is seen that both curves have a sigmoidal shape, in agreement with the prediction made in a previous paper[2]. In addition, they both pass through an inflection point in the range 50 to 60°C. This behavior appears to be in line with the fact that fresh fish muscles are generally coagulated thermally in this region of temperature. It is also observed that addition of soya-bean oil brings about a lowering of the heat conductivity over the temperature range herein investigated. This is expected because the heat conductivity of soya-bean oil is about one third that of water at ordinary temperatures. It is of some interest to note that the heat conductivity of water at 30°C. is 1.47×10^{-3} cal. cm.$^{-1}$ sec.$^{-1}$ °C.$^{-1}$ and that of mackerel with no added oil at the same temperature is, as Figure 3 shows, 1.05×10^{-3} cal. cm.$^{-1}$ sec.$^{-1}$ °C.$^{-1}$ This difference may be accounted for mainly by the water content and the oil content of the sample fish.

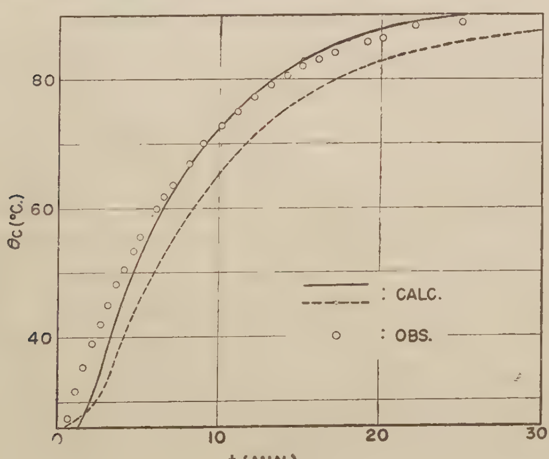


Fig. 4. Comparison of calculated curves with observed values; solid line represents the curve for a variable heat conductivity and dashed line curve for a constant heat conductivity

Finally, the θ_c vs. t curve for $k(\theta)$ represented by the solid line in Figure 3 is calculated directly from the differential equation (1) and com-

pared with the observed data. The solution of Eq. (1) was carried out for the case in which $\theta_0=26°C.$ and $\theta_e=90°C.$, by making use of the graphical method of solution proposed by Osida[4]. The resultant θ_c vs. t curve is plotted in Figure 4 by solid line and is seen to agree well with the observed values indicated by open circles, except in the region of small t. The dashed line in the same figure represents the curve calculated from Eq. (5) by taking for k the value of k at 90°C. Comparison of this with the solid line demonstrates clearly that even such a relatively weak dependence of k on temperature as observed here has a pronounced influence on the rate of increase of temperature at the center of a flat can (probably for cans of other types, too). This results may be of practical significance to those who are engaged in canning processing.

The authors wish to thank Professor T. KAWAKAMI who read the manuscript.

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Studies on Physico-Chemical Properties of Marine Products and Related Substances—VI. Rigidities of Agar Hydrogels*

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Introduction

Agar is known as a prototype of naturally occurring gel-forming high polymeric substances. It is essentially a polyelectrolyte containing HSO_3 and COOH as ionizable groups. As has been shown by NAKAGAWA[1], its aqueous solutions exhibit a measurable elasticity even at as low a concentration as 0.04 %. In a series of papers[2] from this Laboratory, some of the rheological properties of concentrated hydrogels of agar have been reported, in the hope of increasing the understanding of the mechanical behavior of this interesting classical colloid. The work described in the present paper is concerned with the rigidity of agar hydrogels as functions of concentration and temperature, and was undertaken as a supplement to our previous investigations. One of its purposes is to check the elasticity-concentration law as proposed recently by HIRAI[3] for a number of gels of natural and synthetic polymeric substances.

Material and Method

The agar used for the present study was a product of WAKO Pure Chemicals Co.; its curde protein, 1.74 %, ash content, 2.27 %, and intrinsic viscosity in 0.5 N NaCl at 26°C., 2.76 dl./g. It was used as delivered, not purified further.

A weighed amount of the sample powder was dissolved in 50 ml. of distilled water at 100°C. for two hours, with constant stirring. A given volume of the agar sol obtained was poured into the annular gap of a concentric cylinder apparatus mounted in a constant temperature water-bath regulated to 80°C. After covering the sol with liquid paraffin, the bath was cooled down at a rate of 3 to 5°C. per hour to 20°C. in most cases studied. The sol was gelatinized during this process, keeping thermal equilibrium with the surrounding water in the bath. The gel thus formed was allowed to stand overnight at 20°C. and then brought to desired temperatures at which rigidities were to be measured.

The apparatus used was a modified STORMER viscometer equipped with a electrically controlled chainomatic balance system and a stress-recording drum, and is illustrated in Figure 1. The dimensions of the cup and the bob are as follows:

cup: inner diameter 5.00 cm. and depth 6.50 cm.
bob: outer diameter 4.225 cm. and length 5.545 cm.

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* Part V of a series on Mechanical Properties of Concentrated Hydrogels of Agar-agar.

The axis of the bob (rotor) is supported at its ends with iridium-sapphaire pivots, lower one of which is fixed at the bottom of the cup. When the upper pivot is properly adjusted, the bob can rotate very freely. Angular displacement can be given to the gel contained in the annular gap by means of a horizontal bar attached rigidly to the axis of the bob, which is, in turn, rotated by desired amounts by pushing its top through a precision screw unit involving a dial gauge. The angular deflection of the bar can be determined very accurately from the reading of the dial gauge, so far as the region of small enough angles is concerned. When the gel is sheared through the rotation of the bob, the balancing chain is moved downward automatically with the aid of an electric device incorporated in the system until the shearing torque produced in the gel is balanced with the torque applied by the balancing chain. The applied torque can be determined readily from the vertical displacement of the movable end of the balancing chain, which is recorded autographically on a chart mounted on a drum.

Since agar is a polyelectrolyte, it seems desirable to keep its sol or gel from direct contact with brass of which the concentric cylinders are made. For this reason, part of the concentric cylinders with which the gel or sol was to be in contact was coated with phenol formaldehyde resin. It is known that agar gels contract spontaneously their volume due to syneresis, and this may cause slippage of the gel on the inner or outer wall of the annular gap when it is sheared in a concentric cylinder apparatus as employed in this work. To minimize this effect, a number of fine wires (about 0.2 mm. diameter) were cemented along the generating lines of the inner and outer walls of the cylinders.

With the concentric cylinder apparatus designed so that the "end-effect" is absent, the rigidity, G, of the sample gel can be evaluated from the equation:

$$G=\frac{T}{4\pi L\theta}\left(\frac{1}{r_1^2}-\frac{1}{r_0^2}\right), \quad \cdots\cdots (1)$$

where r_0 and r_1 are the radii of the bob and the cup, respectively, L is the depth of immersion of the bob, T is the torque applied around the axis of the bob, and θ is the angular deflection of the bob. According to LEADERMAN[4], when the end effect is present, Eq. (1) may be modified to

$$G=\frac{T}{4\pi (L+\Delta L)\theta}\left(\frac{1}{r_1^2}-\frac{1}{r_0^2}\right), \quad \cdots\cdots (2)$$

where ΔL is a correction to L introduced to take the end-effect approximately into account. Eq. (2) may be rewritten

$$L=\frac{T}{4\pi G\theta}\left(\frac{1}{r_1^2}-\frac{1}{r_0^2}\right)-\Delta L. \quad \cdots\cdots (3)$$

Hence, ΔL may be evaluated by extrapolating the L vs. T curve obtained at a fixed value of θ for gels of constant concentration to zero value of T. For the apparatus used in this work, a value of 0.7 cm. was obtained for ΔL. All rigidity values reported in this paper were derived by determining G for several small enough values of θ and extrapolating the resulting plots to zero θ. Rigidity G for each θ was computed from Eq. (2) with $\Delta L=0.7$ cm.

Results and Discussion

Effect of Temperature.

The effect of temperature upon rigidity was studied only on agar gels of 4 % con-

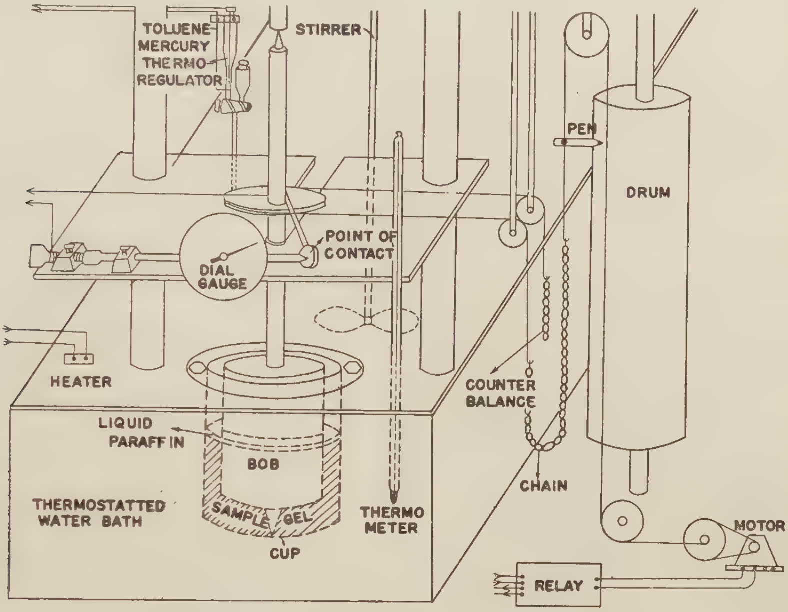


Fig. 1. Schematic view of the concentric cylinder apparatus and accessories

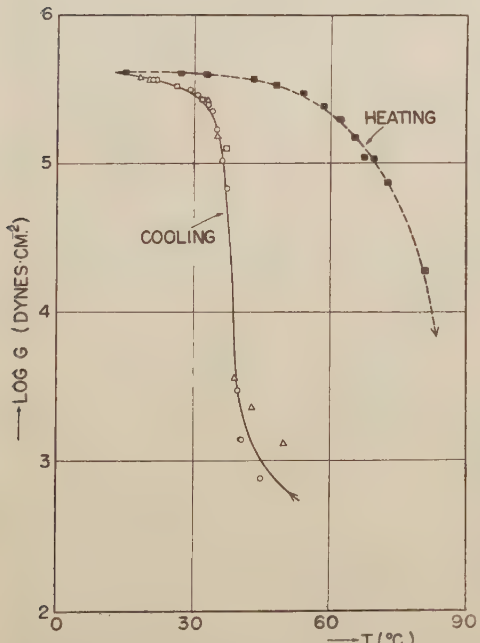


Fig. 2. Rigidity changes upon cooling (solid line) and upon heating (dashed line)

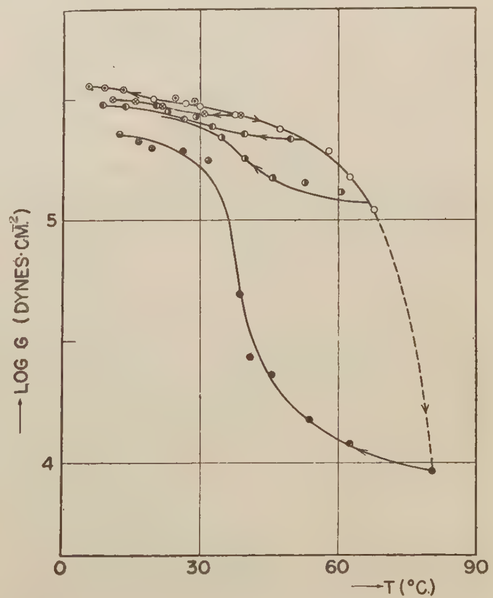


Fig. 3. Temperature dependence of rigidity of 4 % agar hydrogel ; open circles are data obtained on heating, and other symbols are those on cooling. All data, except for those represented by closed circles which were derived with gels formed at 35°C., were obtained with gels prepared at 20°C.

centration. First the change of G with decreasing temperature was followed in triplicate by cooling down a hot sol at a rate of 2 to 4°C. per hour to room temperature (about 15 °C.). The solid line in Figure 2 shows this change on a semi-logarithmic graph; the open circles, triangles, and squares, each representing data from a different run, are seen to agree well each other within experimental error. It is noted from the figure that G increases very sharply when cooling down the sol from 40 to 35°C. This indicates that the sol is gelatinized almost completely in a very narrow range encompassing 37°C. At lower temperatures the rigidity increases much more slowly with decreasing temperature and appears te level off a value of about 4×10^5 dynes/cm.^{2} After the gel had been allowed to stand overnight at 15°C., the temperature of the bath was raised at a rate of 3 to 5°C. per hour, and the subsequent change of G was followed up to 81°C. The dashed line in Figure 2 shows this G change upon heating. It is seen that the process upon heating is entirely different from that upon cooling; no adrupt change in rigidity appears in the vicinity of the gelation temperature as observed in cooling, and instead the curve drops off increasingly sharply as the temperature approaches 90°C. This indicates melting of agar hydrogel to occur in the neighborhood of 90°C., in agrement with the description given in usual textbook on colloid chemistry. The hysteresis of the rigidity-temperature cycle as observed here for a 4 % agar hydrogel is really tremendous, and we have, at present, no adequate molecular interpretation for this phenomenon, although it is supposed to be correlated with an intrinsic polyelectroyte character of agar molecules.

In order to obtain more information about the temperature dependence of rigidity of agar hydrogel, 4 % gels formed at 20°C. were heated, respeciively, to 29, 39, 50 and 68°C. at a rate of 3 to 5°C. per hour and then cooled down to appropriate temperatures at the same rate as in the heating. The values of G measured in these temperature cycles are plotted logarithmically in Figure 3, where the open circles represent data obtained on heating and other symbols are those measured on cooling. The data represented by the closed circles were obtained from a 4 % gel which was formed at 35°C., heated to 81°C. and then cooled down at the same rate as for the others. It is noted from Figure 3 that the hysteresis of the rigity-temperature loop becomes marked as the highest temperature in the cycle is increased and appears to tend the shape illustrated in Figure 2 in the limit when the gel is melted to a complete sol. NAKAGAWA and DANNO[5] reported that sor 0.15 % agar hydrogels no hysteresis was observed in the rigidity-temperature cycle up to temperatures near the melting point. The large discrepancy of our results

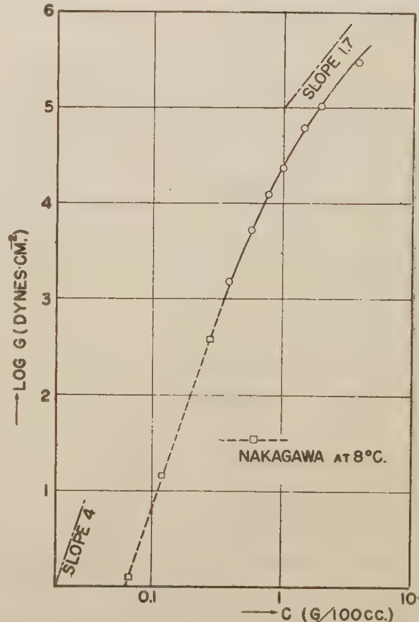


Fig. 4. Concentration dependence of rigidity for agar hydrogel at 30°C.; gels used for measurements were formed at 20°C.

with theirs may partly be attributed to the difference of gel concentration in both studies. However, there is no doubt that more detailed investigations are indicated on this point, in view of the fact that the rigidity-temperature hysteresis in concentrated agar gels is unusually large compared with those in other polymeric gels of comparable concentrations.

Effect of Concentration.

For a series of agar hydrogels of concentrations ranging 0.4 to 4.0 %, all formed at 20°C. and allowed to stand overnight before measurements, rigidities were determined at 30°C., and the results are plotted in Figure 4 on a log-log graph. In the figure, the open circles represent the present experimental data, while the squares are the values obtained by NAKAGAWA[1] at 8°C. and included for comparison. Our data appear to be connected quite smoothly to NAKAGAWA's data below the lowest concentration at which the present measurement was made, despite the fact that both data were obtained at different temperatures. This agreement is probably somewhat fortuitous; however, it is not necesarily an unexpected one, considering that, as demonstrated in Figure 3, the temperature dependence of G at temperatures below about 30°C. is practically negligible when G is plotted on a logarithmic scale. At concentrations higher than 2 % the data follow a straight line having a slope of 1.7, in complete agreement with our previous finding from compression experiments.[2a] HIRAI[3] has recently reported that for number of both natural and synthetic gels there can be observed in their rigidity-concentration curves a distinct break, above which the rigidity increases with the second power of concentration, and below which the rigidity is proportional to the fourth power of concentration. From the data presented in Figure 4, it can be seen that G is proportional to C^4 in the region of sufficiently small concentrations, in exact agreement with HIRAI's statement, and increases with $C^{1.7}$ at high enough concentrations, in approximate conformity with HIRAI's law. Although HIRAI reported the break in the rigidity-concentration curve for agar hydrogel to appear at a concentration of 0.85 %, there is observed in our data no such break but the curve is continuous everywhere in the entire concentration range herein studied. Accordingly, it is concluded that HIRAI's rigidity concentration law, though very useful practically, is not strictly valid if rigidity data are determined more accurately than those on which his deduction was based.

The authors wish to express their thanks to Professor H. FUJITA for his interest and help in the course of this work. Thanks are also due Mr. T. MAKI, former member of this Laboratory, for his aid in constructing the apparatus.

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カツオ幽門垂の利用に関する研究—I.*
幽門垂エキスよりヒスチジンの分離

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Studies on the Utilization of Pyloric Coeca of Skipjack—I. Preparation of Histidine from Pyloric Coeca Extract

Daiichi KAKIMOTO and Hiroshi MIZUMA

In order to prepare the histidine from the extract in pyloric coeca of skipjack, Japanese acid clay was used as adsorvent. Adsorbed histidine was eluted from acid clay and precipitated with Hopkins-Cole reagent.

The yield of histidine thus obtained corresponded to 64 per cent by the bioassay value.

カツオ幽門垂エキスには数多くのアミノ酸が遊離状態で含有されているが，そのうちヒスチジンは必須アミノ酸として栄養的に最も重要なものゝ一つであるのでその分離を試みた。天然物中から個々のアミノ酸を分離する方法については多くの研究があるがその多くは蛋白質の酸又はアルカリによる分解物からの分離法である。然るに著者等が材料にしようとする幽門垂エキスには，アミノ酸以外に色々の種類の含窒素成分[1)2)]が含まれているため，従来行われて来ている燐タングステン酸処理による方法ではヒスチジン以外の有機塩基類の混入によつてその純粋分離が可成り困難であるし，又昇汞を使用する方法も存在するオルニチンの沈澱によつて妨げられる。著者等は以上の困難にかんがみ，ヒスチジンを撰択的に他の物質から分けるために酸性白土による吸着法を応用することを試み，一応目的を達することができたのでその方法を報告する。

実験の部

1. 試料及び使用試薬

試料はカツオ幽門垂の熱水抽出液をシラップ状まで濃縮したもので，その水分含量は64%であつた。用いた主な試薬は中性酢酸鉛，炭酸銅，ピクリン酸，酸性白土，Hopkins-Cole 試薬などで，前三者は市販品そのまゝ，酸性白土は次の様な活性化の処理を施したものを用いた。即ち市販の酸性白土 100 g を 2 %酢酸 200 cc に浸漬し，約1時間振盪した後遠心分離によつて酢酸から分ち，次に 4 %苛性ソーダ 200 cc を加えて約1時間振盪した後同じく遠心分離し，リトマス紙に対し中性になるまで蒸溜水で充分洗滌して水を切り 120°C の空気浴中に約4時間乾燥した後乳鉢で細粉とした。

2. 幽門垂エキスよりヒスチジンの分離精製工程

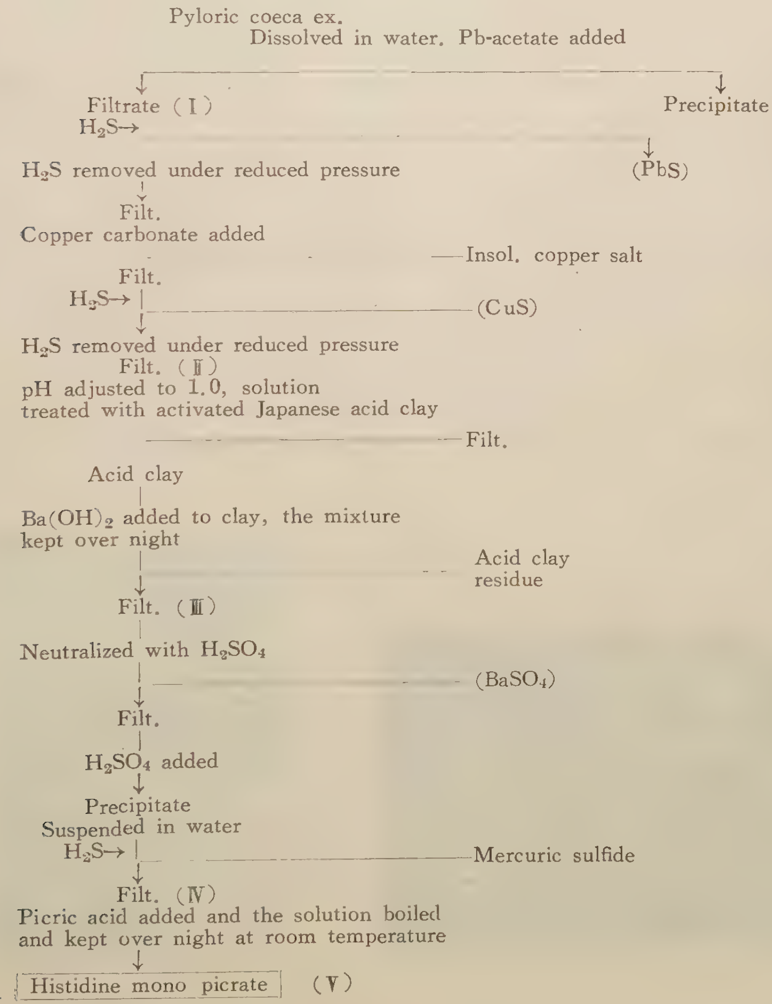
最初 KOSSEL, KUTSCHER 等の方法による分離を試みたが成功しなかつたので酸性白土吸着法について研究した。この方法はまずヒスチジンを選択的に酸性白土に吸着させた後，Hopkins-Cole 試薬によつて共に吸着された少数の他物質から分別することを骨子とするものである。前記の幽門垂エキス 500 g を蒸溜水約 1 l に溶解し，少量の不溶物質を濾別した後 25 %酢酸鉛液を加え一夜放置後遠心分離によつて沈澱物を除去した溶液に硫化水素を通じて鉛を除き，更に硫化水素を蒸溜除去した後過剰の炭酸銅を加えてアミノ酸の銅塩を作り，その際生成した不溶性銅塩を濾別除去した後硫化水素によつて銅を除き，減圧下に濃縮して全容を約 200 cc とする。この溶液は pH 4.5 を示したがこれに 5 %硫酸を加えて pH を 1.0 となした後 30 g の酸性白土を加え室温に約3時間振盪する。この白土による吸着操作を数回反覆し，毎回の白土を合して蒸溜

1956 年 3 月 20 日受理

*1955 年 4 月 日本水産学会大会に講演

水で洗滌した後 300 cc の蒸溜水中に分布し，水酸化バリウム溶液を加え室温に一夜放置する。この間時々攪拌して被吸着物質の溶出を促す。これによつて溶液は次第に黄褐色を呈し一方白土は灰白色となる。かくして溶離を終つた溶液に硫酸を加えて存在するバリウムを定量的に除去し，全容を約 100 cc に濃縮，これに Hopkins-Cole 試薬を加えると黄褐色の沈澱を生ずる。この沈澱はヒスチジンの水銀塩と思われるものであるが沈澱を完全ならしめるために一夜放置する。更にこれを精製するために水に分布せしめ硫化水素を通じて分解し，水銀を除いた後減圧下に濃縮し pH を 4.5 に調整してピクリン酸の飽和水溶液を加え，一旦煮沸した後低温に放置すれば針状の結晶が析出する。その収量は 1.5 g であつた。これを温水より再結晶して得た 1.3 g のピクレートは融点 80°C，ガンニング変法による全窒素量 23.4 %で，ヒスチジンのモノピクレートに相当することが分つた。更に常法によりこのピクレートを塩酸塩にかえ試験した結果その融点は 251.3°C で，ヒスチジンモノ塩酸塩にほゞ一致し，一方濾紙クロマトグラムによつてもヒスチジンであることが確認された。なお以上の分離法によるヒスチジンの収量を知るため，試料エキス中のヒスチジンを ***Lactobacillus fermenti*** を用いる Bioassay 法によつて定量した結果，エキス乾物 1 g 中 27.5 mg であつたが，これによつて計算すると約 65 %の収量となる。次の Diagram はヒスチジン分離の工程を示したものである。

Diagram 1. General scheme for separation of histidine



3. ヒスチジン分離過程におけるアミノ酸の分配

前記著者等の方法によつてヒスチジンの分離を行う場合，試料エキス中に存在するアミノ酸類が各操作の過程において如何なる態度をとるかを調べた結果は Table 1 の通りであつた。これは前記の各操作毎に濾紙クロマト法により処理液のアミノ酸を検索したもので，その検出にはニンヒドリンとジアゾ試薬を用いた。表に見られるように本分離方法中，pH 1.0 に於て酸性白土処理を行う工程は大多数のアミノ酸を除き得る点で極めて有効な処理ということができ，この条件で白土に吸着され，バリタで溶離されるものはヒスチジン，アルギニン，バリン，ロイシンの四者のみで，この4アミノ酸から Hopkins-Cole 試薬によつてヒスチジンのみを沈澱分離するわけである。尚 Fig. 1, 2 は著者の分離したヒスチジンである。

Table 1. Amino acids found in the process of histidine separation

Amino acid	Process				
	I	II	III	IV	V
Histidine	+	+	+	+	+
Aspartic acid	+	−	−	−	−
Glutamic acid	+	+	−	−	−
Cystine	+	+	−	−	−
Serine	+	+	−	−	−
Glycine	+	+	−	−	−
Threonine	+	+	−	−	−
Alanine	+	+	−	−	−
Tyrosine	+	+	−	−	−
Valine	+	+	+	−	−
Leucine	+	±	±	−	−
Phenyl alanine	+	±	−	−	−
Lysine	+	+	−	−	−
Proline	+	+	−	−	−
Arginine	+	+	+	−	−
Ornithine	+	+	−	−	−

Process I, II, III, IV and V are same as those of Diagram 1.

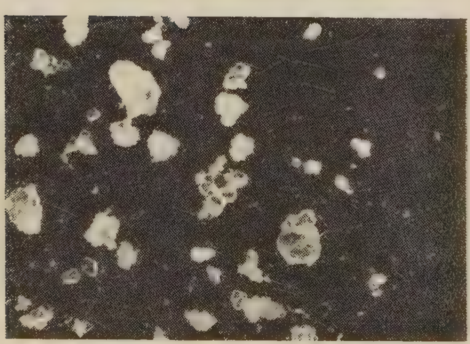


Fig. 1. Histidine mono-hydrochioride

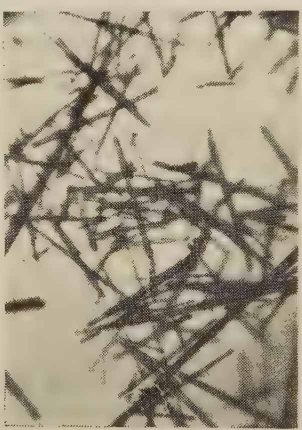


Fig. 2. Histidine mono-picrate

摘　　要

カツオ幽門垂エキスからヒスチジンを分離する方法を研究し，酸性白土吸着法によつて他の大多数のアミノ酸類から分け，更に Hopkins-Cole 試薬を用いてヒスチジンを汞銀塩として分離することができた。本法によるヒスチジンの収量は試料に存在する全ヒスチジンの約 64 %であつた。

本研究に当り終始御指導を賜つた本学柏田研一教授に深謝する。なお本研究費の一部は文部省科学研究費によつた。

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カツオ幽門垂の利用に関する研究—II*.
幽門垂エキスよりアルギニンの分離

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Studies on the Utilization of Pyloric Coeca of Skipjack—II. Preparation of Arginine from Pyloric Coeca Extract

Daiichi KAKIMOTO and Tetsuro YOSHIMINE

In the isolation of arginine from extractive matter of pyloric coeca, it is necessary to find means for elimination of agmatine. Basic nitrogen compounds containing arginine and agmatine were separated from other matters by the treatment with activated charcoal at pH 8.0 followed by the elution with HCl-acetone. After removed of acetone the residue was treated with picric acid, almost all the agmatine being precipitated. After filtering off the agmatine picrate, arginine was precipitated as its flavianate, and finally purified as the hydrochloride. The yield of arginine thus obtained corresponded to 76% by the bioassay value.

著者等は前報[1]に於て幽門垂エキスよりヒスチジンの分離に関する研究を報告したが，引続きアルギニンの分離を試みた。アルギニンの分離に就いては種々の方法が考えられるが，第1報で報告したように試料が蛋白質の加水分解物ではないため，夾雑するアミノ酸以外の物質の影響を考慮しなければならない。特に幽門垂エキス中にはアグマチン，アルカインその他アルギニン類似の有機塩基が数多く含まれていることは著者の一人が既に報告[2]した処である。これ等の化合物は当然アルギニンの分離に影響を与えることが考えられるので古くから行われているゼラチン酸水解物よりの分離法[3]そのまゝを適用することはできない。著者等はアルギニン及びその類似化合物を特定の pH 条件下で活性炭吸着を行うことにより比較的容易に他のアミノ酸類から分別し，更に共存するアグマチンは大部分をピクレートとして除去し得ることを知つたのでこのことを応用してアルギニンを分離することができた。以下その方法並にこれにともなう共存物質の影響について報告する。

実 験 の 部

1. 試料： 試料は第1報[1]と同様 64% 含水の幽門垂エキスを用いた。

2. 試薬の調製： アルギニン分離のための沈澱試薬として中性酢酸鉛，ピクリン酸，フラビアン酸の三者，吸着用に活性炭，脱着用に酸性アセトン溶液等を使用したが，活性炭及び酸性アセトン溶液は次の如く調製した。

a. 石津製活性炭 50g に N-HCl 500cc を加え，湯煮上で攪拌しつゝ約5時間加温後，熱時上澄を傾瀉し，次いで熱蒸溜水で Cl イオンの消失するまで洗滌を繰返し，乾燥後，更に 120°C に4時間加熱したものを使用した。

b. 塩酸々性アセトン溶液は 80% アセトン液に 10% の塩酸を加えて pH を 2.0 としたもので，活性炭に吸着せしめたアルギニンの脱着に使用した。

3. 幽門垂エキスよりアルギニン分離方法： 前記のカツオ幽門垂エキス 200g に蒸溜水を加えて全体を約 1 *l* に稀釈し，不溶物を濾別する。この溶液に 25% 中性酢酸鉛溶液を加えて沈澱を完成せしめ一夜放置後沈澱を濾別し，濾液部に硫化水素を通じて鉛を除去した後減圧濃縮して硫化水素を溜去する。該溶液のpHは

1956 年 3 月 20 日受理
* 1956 年 4 月 日本水産学会にて講演

5.6を示したので稀塩酸により pH 5.0 となした後活性炭を加えて脱色し，次に10%のカセイソーダを加えて pH を 8.0 とする。アルギニンその他の塩基性窒素化合物はこの pH 条件で良く活性炭に吸着されるので溶液が坂口反応を呈しなくなる迄活性炭を取り替えて吸着を繰返す。吸着を終えた活性炭を合し冷水で2～3回洗滌した後真空乾燥し微粉末状とする、次にその 1g に対し前記の酸性アセトン溶液 25cc を加えて 30分間振盪する溶出操作をくり返す。玆に得た抽出液を合し，減圧濃縮しアセトンを除去する。該溶液中にはアルギニンの他アグマチン等のグアニジン体，リヂン等数種のアミノ酸類が含まれている（Table 1 参照)。この溶液に直ちにフラビアン酸を加えて煮沸放冷するとアルギニンとアグマチンの混合フラビアネートを

Table 1. Amino acids found in the process of arginine separation

Amino acids or bases	Process 1	2	3	4	5
Arginine	+	+	+	+	+
Aspartic acid	+	±	−	−	−
Glutamic acid	+	+	−	−	−
Cystine	+	+	+	−	−
Serine	+	+	−	−	−
Glycine	+	+	−	−	−
Threonine	+	+	−	−	−
Alanine	+	+	+	+	−
Tyrosine	+	±	−	−	−
Valine	+	+	+	+	−
Leucine	+	+	+	+	−
Phenyl alanine	+	+	+	+	−
Lysine	+	+	+	−	−
Histidine	+	+	+	+	−
Proline	+	+	−	−	−
Ornithine	+	+	−	−	−
Agmatine	+	+	+	−	−
Arcaine	+	+	+	−	−
Methyl guanidine	+	+	+	−	−
Octopine	−	−	−	−	−
Unknown	+	+	−	−	−

Process 1, 2, 3, 4 and 5 are same as those diagaram 1.

析出しアグマチンの離脱ができないが，あらかじめピクリン酸飽和水溶液を加えて煮沸放冷すると，大部分のアグマチンをピクレートとして除去することができる。このようにしてアグマチンをピクーレトとして濾別した後フラビアン酸を加え，湯煎上で加温して充分にフラビアン酸を溶解し室温に放置すると無定形のアルギニンフラビァネートを得る。これを濾別し，冷水で充分に洗滌した後熱水に溶解し放冷してアルギニンフラビァネートを再結晶せしめる。斯くしてアルギニンフラビァネート 2.5g を得た。このものは融点253°Cで黒変，270°C で分解しアルギニンモノフラビァネートと一致したが，更に玆に得たフラビァネートを常法[4]により分解し塩酸塩として結晶せしめた。その収量 0.82g 融点 217°C，分解点 235.4°C，全窒素21.2%で武田製アルギニン一塩酸塩と一致した。Fig. 1 は著者の分離せるアルギニンである。更に又ブタノール，酢酸，水（4：1：1）を展開剤とする濾紙クロマト法により同定の結果 Rf 値 0.18 を示し，フェノール，水（25%含水）による Rf 値 0.61 でニンヒドリン，坂口両反応を与え，これによつても全くアルギニンと一致することが確認せられた。

4. 幽門垂エキスのアルギニン含有量： 前述の如き方法で幽門垂エキス中からアルギニンを単離することに成功したが，分離法としては収量を考慮する必要があるので試料エキス中のアルギニンを *Lactobaci-*

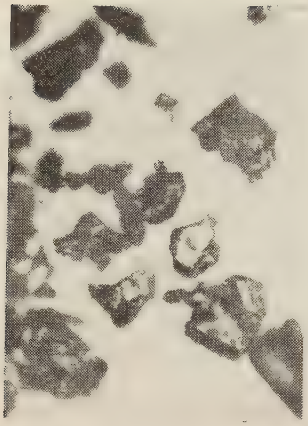


Fig. 1. Arginine mono-hydrochloride

llus arabinosus による bioassay 法で定量した。即ち試料エキスから酢酸鉛による沈澱を除いた濾液に硫化水素を通じて鉛を除去した後 pH 6.8 に調整し，assay の試料にした。測定の結果エキス乾物 100 g 中 1.85 g の遊離アルギニンが存在することを知つた。なお試料を加水分解したものでは 2.12 g であつた。前述の分離実験では試料 200 g を使用しフラビアネートとして 2.5 g を得たのでアルギニンとしては 0.88 g に該当し，なおこれは供試エキスに含まれる総アルギニンの約 76 % に相当する。分離法の概要を示すと Diagram 1. の通りである。

5. アルギニン分離過程に於ける各成分の分配： 前記著者等の方法に従つて幽門垂エキスよりアルギニンを分離する場合，各処理工程に於てアルギニン，及びその他試料中の窒素化合物が如何に分配され又は脱落するかを濾紙クロマト法により追及した。結果は Table 1 の通りである。なお各物質の検出はニンヒドリン反応と坂口反応によつた。前記の分離操作を少くし吟味するに，まず pH 5.0 に於いて一且活性炭処理を行つたが，この活性炭を pH 8.0（バリタを使用）に於て 80 % アセトンで溶離試験したところ，その中にチロジン，ゼリン，アスパラギン酸を認めたがアルギニンは検出されなかつた。即ち pH 5.0 於ける活性炭処理でアルギニンは吸着されない。次に pH 8.0 に於て吸着せしめた活性炭を pH 2.0 の酸性アセトン溶液で抽出した部分には，オクトピンとメチルグアニジンが新たに検出されたがこれは之等の物質が処理中に新生したものか或いは濃縮によつて現われたものかは明確には知り得なかつた。又アルギニンとアグマチンの混在しているものにフラビアン酸を加えると常に両物質が共に不溶性のフラビアネートとして析出することが濾紙クロマトによつて知られた。更にアルカリ性に於て活性炭に吸着された部分にピクリン酸を加えて不溶性のピクレートを作

Diagram 1. General scheme for separation of arginine

Pyloric coeca ex.
↓
Dissolve the extract in 1 liter of water. Add Pb-acetate
→ Filtrate | Precipitate

Filtrate
H_2S→
→ Filtrate (1) | (PbS)

Filtrate (1)
↓
Remove H_2S under reduced pressure
↓
After adjusting the pH at 5.0 treat the solution with charcoal
→ Filtrate | Charcoal

Charcoal
↓
Wash the charcoal with 80 % acetone-water
→ Eluate (3) | Charcoal

Eluate (3)
↓
Distil off the acetone. Add sat. picric acid
→ Insol. picrate | Soluble picrate (4)

Soluble picrate (4)
↓
Add flavianic acid and keep at room temperature
↓
Arginine flavianate (5)

り，常法により分解し濾紙クロマトを行つてみたところ之等の中にはアグマチン，リジン，シスチン，アルカイン，メチルグアニジンが含まれていた。依つてアルギニンからアグマチンを除去するためには前処理としてピクレートを作る必要があることを確かめた。

要　　約

カツオ幽門垂エキスからアルギニンを分離するためには共存するアグマチンの除去が必要である。そのための前処理として pH 8.0 で活性炭に吸着せしめた両者を酸性アセトンにより溶出し，これにピクリン酸を加えて共存するアグマチンをピクレートとして除去した後アルギニンをフラビァネートとして他の夾雑物から分離する方法を考案した。本法によつてカツオ幽門垂エキス中のアルギニンを約 76％ の収量を以て分離することができた。

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